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The Kinetic Energy of Polyatomic Molecules

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The theory of rotating axes and polyatomic molecules is extended in a form applicable to linear and anomalous molecules. It is applied to a linear tetratomic molecule and to an anomalous ammonia-like molecule, to obtain, in each case, a Hamiltonian kinetic energy lacking first-order terms. A second-order perturbation calculation yields the energy of interaction between rotation and vibration for the linear molecule. The relationship to Howard's theory of ethane is also given.

INTRODUCTION

THE systematic theory of the motion of polyatomic molecules referred to moving axes has been developed by Eckart[1] for the case of nonlinear normal molecules. In this theory, the unique definition of the axes is provided by certain conditions on the coupling terms[2] in the kinetic energy, which were suggested by Casimir's[3] study of rigid bodies in quantum mechanics. It is possible, however, to treat the interaction of rotation and vibration from a more general viewpoint, such as that considered by Welker,[4] which is applicable to linear molecules, and to various types of anomalous molecules as well. For the purposes of application, this general theory may be specialized so that it assumes a form similar to the method of rotating axes, and for nonlinear normal molecules, is, in fact, identical with it. In illustration, the method is applied to a linear tetratomic molecule and to an anomalous molecule like ammonia.

[1] C. Eckart, Phys. Rev. **47**, 552 (1935).
[2] See also, H. A. Jahn, Ann. d. Physik **23**, 529 (1935).
[3] H. B. G. Casimir, *The Rotation of a Rigid Body in Quantum Mechanics*. Dissertation, Leyden (1931).
[4] H. Welker, Zeits. f. Physik **101**, 95 (1936).

THE GENERAL METHOD

Many polyatomic molecules are known to behave like approximately rigid bodies while still others possess only one or two degrees of internal freedom. Thus, it might be said that a general N atomic molecule consists of approximately rigid parts which may move relative to each other while the whole structure translates and rotates freely through space. Let it be assumed, for the time being, that the parts are perfectly rigid and that their relative motion is unconstrained. The system is thus in neutral equilibrium since it follows that the potential energy is identically zero. To specify the position in space of the equilibrium configuration defined in this way, fewer than $3N$ coordinates are needed, and these may be taken to be of two types: (a) six (or five) coordinates α', whose variation describes the over-all translation and rotation of the molecule, and (b) one or more coordinates α'' which describe the gross internal motions.

The equations of transformation from cartesian coordinates,

$$x_k = F_k(\alpha_p),$$

$k=1, 2, \cdots, 3N; p=1, 2, \cdots, M<3N$, are simply the equations of rigid constraint under which the motion takes place, and this will be termed the "rigidly constrained" motion. It is convenient to let the x_k represent the coordinates of an atomic particle multiplied by the square root of its mass, and to use (in this section only) the summation convention. The properties of the system, in both classical and quantum mechanics, depend upon the Hamiltonian, which is readily obtained:

$$\begin{aligned}\dot{x}_k &= (\partial F_k/\partial\alpha_p)\dot{\alpha}_p \\ 2T &= \Sigma\dot{x}_k^2 \\ &= \Sigma_k(\partial F_k/\partial\alpha_p)(\partial F_k/\partial\alpha_r)\dot{\alpha}_p\dot{\alpha}_r,\end{aligned}$$

which may be written:

$$2T = A_{pr}^{(0)}\dot{\alpha}_p\dot{\alpha}_r.$$

The Hamiltonian is then

$$2H = A_0^{pr}P_pP_r,$$

where the matrix A_0^{pr} is the reciprocal of $A_{pr}^{(0)}$, and P_p is conjugate to α_p. Since the solution of the characteristic value problem for this Hamiltonian is known in most cases, the rigidly constrained motion can be considered as part of the zeroth-order approximation to the true motion.

To secure a more accurate molecular model, the atoms hitherto supposed to constitute one of the rigid parts must be allowed to vibrate about their equilibrium positions but, as a first approximation, with very small amplitudes, so that the configuration departs only slightly from the rigid structure. If the $3N-M$ additional degrees of freedom, q_λ, are introduced in the form:

$$x_k = F_k(\alpha_p) + f_{k\lambda}(\alpha_p)q_\lambda, \tag{1}$$

$\lambda=1, 2, \cdots, 3N-M$, so that they describe the deviation from equilibrium, and the zeroth-order potential energy is written as a (positive definite) quadratic form in the q_λ:

$$2U_0 = b_{\lambda\mu}(\alpha'')q_\lambda q_\mu, \tag{2}$$

the motion will have the desired characteristics. Thus, Eq. (1) represents a loosening of the rigid constraints, and the motion might now be described as the "elastically constrained" motion. The solution of the "elastic constraint" problem enables the prediction of the major features of the molecule's infra-red spectrum.

As usual, the Hamiltonian must be computed. The velocities are:

$$\dot{x}_k = [\partial F_k/\partial\alpha_p + (\partial f_{k\lambda}/\partial\alpha_p)q_\lambda]\dot{\alpha}_p + f_{k\lambda}\dot{q}_\lambda,$$

and the Lagrangian kinetic energy has the form:

$$2T = A_{pr}\dot{\alpha}_p\dot{\alpha}_r + 2B_{p\lambda}\dot{\alpha}_p\dot{q}_\lambda + C_{\lambda\mu}\dot{q}_\lambda\dot{q}_\mu, \tag{3}$$

in which the coefficients A_{pr} have the form: $A_{pr}^{(0)} + A_{pr\lambda}q_\lambda + A_{pr\lambda\mu}q_\lambda q_\mu$. The first group of terms in (3) constitutes the energy of the system under the constraints q_λ = constant, and includes the energy of translation and rotation; the third sum is the kinetic energy of vibration, while the second represents the energy of interaction between rotation and vibration.

It is desired, first, that the interaction terms be small enough to be considered as a perturbation of second order or higher, and second, that the q_λ be the normal coordinates. To see how the first requirement, which is a generalization of what has been called Casimir's condition,[1, 3] can be effected, consider the explicit form of the $B_{p\lambda}$, which is

$$B_{p\lambda} = (\partial F_k/\partial\alpha_p)f_{k\lambda} + (\partial f_{k\mu}/\partial\alpha_p)f_{k\lambda}q_\mu,$$

or, for short,

$$B_{p\lambda} = B_{p\lambda}^{(0)} + B_{p\lambda\mu}q_\mu.$$

If, as usual, one sets

$$B_{p\lambda}^{(0)} = 0, \tag{4}$$

the $B_{p\lambda}$ will be small for small vibrations. These may be considered as equations partially determining the $3N(3N-M)$ functions $f_{k\lambda}$. Since there are M equations for each value of λ, $3N-M$ of the $f_{k\lambda}$ remain arbitrary. These are determined by the solution of the normal vibration problem in the $3N-M$ coordinates q_λ as follows. The potential energy,

$$U(x_k) = U(F_k + f_{k\lambda}q_\lambda),$$

may be expanded in a Taylor's series about the equilibrium values of the coordinates:

$$\begin{aligned}U &= \tfrac{1}{2}(\partial^2U/\partial x_k\partial x_l)_{x=F}f_{k\lambda}f_{l\mu}q_\lambda q_\mu + \cdots \\ &= \tfrac{1}{2}\beta_{kl}f_{k\lambda}f_{l\mu}q_\lambda q_\mu + \cdots,\end{aligned}$$

this being a definition of β_{kl}. The $b_{\lambda\mu}$, (Eq. (2)), are therefore,

$$b_{\lambda\mu} = \beta_{kl}f_{k\lambda}f_{l\mu},$$

while the $C_{\lambda\mu}$, (Eq. (3)), are readily verified to be

$$C_{\lambda\mu}=f_{k\lambda}f_{k\mu}.$$

The remaining $f_{k\lambda}$ are then uniquely determined by the conditions:

$$b_{\lambda\mu}=0 \quad (\lambda\neq\mu), \tag{5}$$

$$C_{\lambda\mu}=A_\lambda(\alpha_p)\delta_{\lambda\mu}, \tag{6}$$

where the A_λ are any preassigned functions.

The explicit definition of the α_p depends on the particular type of molecule to which the method is to be applied, and for this purpose, normal and anomalous molecules may be distinguished, and discussed separately.

Normal Molecules

A molecule which, in the vibrationless state (neglecting zero-point energy), behaves like a completely rigid body may be called normal. If it is nonlinear, the α_p are six in number ($M=6$), and are most conveniently chosen to specify the position in space of a set of axes moving with the molecule, namely; the three components, X, Y, Z, of the vector $\mathbf{R}$ to the origin, and the three Eulerian angles,[5] θ, ϕ, ψ, of the axes. Let the unit vectors along the moving axes be $\boldsymbol{\varepsilon}_i$ remembering that these are functions of the Eulerian angles. Also, let the index k of Eq. (1) be an abbreviation for two indices, i, a, ($i=x, y, z$; $a=1, 2, \cdots, N$), so that x_{ia} are the coordinates of the ath atom in fixed axes. If $\mathbf{e}_i$ are the fixed unit vectors, the rigid constraints, $F_k(\alpha_p)$, become

$$F_{ia}=m_a^{\frac{1}{2}}(\mathbf{R}+\mathbf{z}_a)\cdot\mathbf{e}_i,$$

where $\mathbf{z}_a(=\Sigma_i z_{ia}\boldsymbol{\varepsilon}_i)$ specifies the equilibrium position of the ath atom in the moving axes.

It will now be shown that, for this case, the method can be reduced to the method of rotating axes. Adopting the notation of reference 1, let the $f_{k\lambda}$ of Eq. (1) have the form

$$f_{ia\lambda}=(\Sigma_j z_{\lambda ja}\boldsymbol{\varepsilon}_j)\cdot\mathbf{e}_i, \tag{7}$$

where $j=x, y, z$, and the $z_{\lambda ja}$ are constants to be determined by Eqs. (4), (5) and (6). Eq. (1) becomes

$$x_{ia}=[m_a^{\frac{1}{2}}\mathbf{R}+\Sigma_j(m_a^{\frac{1}{2}}z_{ja}+\Sigma_\lambda z_{\lambda ja}q_\lambda)\boldsymbol{\varepsilon}_j]\cdot\mathbf{e}_i. \tag{8}$$

If y_{ia} stands for the cartesian coordinates of the ath atom in the moving axes, multiplied by $m_a^{\frac{1}{2}}$, it is also true that

$$x_{ia}=[m_a^{\frac{1}{2}}\mathbf{R}+\Sigma_j y_{ja}\boldsymbol{\varepsilon}_j]\cdot\mathbf{e}_i.$$

Hence, by comparison with Eq. (8),

$$y_{ja}=m_a^{\frac{1}{2}}z_{ja}+\Sigma_\lambda z_{\lambda ja}q_\lambda,$$

which is the conventional transformation of coordinates. It remains to be proved that the six equations, $B_{p\lambda}{}^{(0)}=0$, are precisely the ones used to define the rotating axes.

Notice, first, that for $\alpha_p=X, Y, Z$, $B_{p\lambda\mu}=0$, so that $B_{p\lambda}{}^{(0)}=0$ implies $B_{p\lambda}=0$. But since this is the condition that the kinetic energy of translation be separable, the three equations $B_{X\lambda}=0$, etc., must be equivalent to

$$\Sigma_a m_a\mathbf{r}_a=0, \tag{9}$$

where $\mathbf{r}_a$ is the position vector in the moving axes, i.e., the origin of these axes is always at the centroid of the molecule. That the equations do have this form can also be proved. The remaining three equations may now be found. For $\alpha_p=\theta$, for example,

$$\partial F_{ia}/\partial\theta=m_a^{\frac{1}{2}}[z_{za}c''\boldsymbol{\varepsilon}_x-z_{za}s''\boldsymbol{\varepsilon}_y+(z_{ya}s''-z_{xa}c'')\boldsymbol{\varepsilon}_z]\cdot\mathbf{e}_i.$$

In this expression, and in what follows, s, c, $=\sin\theta$, $\cos\theta$; s', $c'=\sin\phi$, $\cos\phi$; s'', $c''=\sin\psi$, $\cos\psi$. Thus, $\partial F_{ia}/\partial\theta$ and $f_{ia\lambda}$ (Eq. (7)) are the ith components in the fixed axes of certain vectors whose components in the moving system are the coefficients of $\boldsymbol{\varepsilon}_i$ in the respective expressions for $\partial F_{ia}/\partial\theta$ and $f_{ia\lambda}$. Since the $B_{p\lambda}{}^{(0)}$ are the sums of scalar products of these vectors resolved along $\mathbf{e}_i$, they can be written in terms of the other components as well, giving:

$$B_{\theta\lambda}{}^{(0)}=\Sigma_a m_a^{\frac{1}{2}}[z_{\lambda xa}z_{za}c''-z_{\lambda ya}z_{za}s''+z_{\lambda za}(z_{ya}s''-z_{xa}c'')].$$

On rearrangement, this becomes:

$$\Sigma_a m_a^{\frac{1}{2}}(s''\mathbf{z}_a\times\mathbf{d}_{a\lambda}\cdot\boldsymbol{\varepsilon}_x+c''\mathbf{z}_a\times\mathbf{d}_{a\lambda}\cdot\boldsymbol{\varepsilon}_y),$$

where $\mathbf{d}_{a\lambda}=\Sigma_j z_{\lambda ja}\boldsymbol{\varepsilon}_j$. In like manner,

[5] The definition of the Eulerian angles to be used here is that of E. T. Whittaker, *Analytical Dynamics* (Cambridge, third edition, 1927), p. 10.

$$B_{\phi\lambda}^{(0)}=\Sigma_a m_a^{\frac{1}{2}}(sc''\mathbf{w}_{a\lambda}\cdot\boldsymbol{\varepsilon}_x-ss''\mathbf{w}_{a\lambda}\cdot\boldsymbol{\varepsilon}_y-c\mathbf{w}_{a\lambda}\cdot\boldsymbol{\varepsilon}_z)=0$$

$$B_{\psi\lambda}^{(0)}=\Sigma_a m_a^{\frac{1}{2}}\mathbf{w}_{a\lambda}\cdot\boldsymbol{\varepsilon}_z=0,$$

in which $\mathbf{w}_{a\lambda}=\mathbf{z}_a\times\mathbf{d}_{a\lambda}$. These three equations imply that

$$\Sigma_a m_a^{\frac{1}{2}}\mathbf{z}_a\times\mathbf{d}_{a\lambda}=0, \tag{10}$$

which is Casimir's condition in vector form,[6] since $\mathbf{d}_{a\lambda}$ has the dimensions $m^{\frac{1}{2}}\times$length.

The normal coordinate problem may likewise be reduced to the conventional one. The $b_{\lambda\mu}$ (Eq. (2)) are simply constants and all the A_λ can thus be set equal to the same normalization constant, A.

Linear molecules

If the equilibrium configuration of the molecule is linear, only five coordinates are necessary to specify its rigid motion: X, Y, Z, θ and ϕ, and there must be $(3N-5)q_\lambda$. Hence, there are only five of the Eqs. (4), which are insufficient to define a set of moving axes uniquely. If, now, the transformation (8) is made exactly as in the preceding section, the angle ψ enters as an arbitrary parameter, which may therefore be set equal to zero, completing the definition of the axes.

The choice of the two Eulerian angles, θ and ϕ, as "rigid constraint" variables implies that $\boldsymbol{\varepsilon}_z$ passes through the equilibrium configuration, which can always be required to have its center of mass at the origin, so that

$$z_{xa}=z_{ya}=0$$
$$\Sigma_a m_a z_{za}=0.$$

In the next section, this method is applied to a general tetratomic linear molecule; the results obtained there may be of use in the interpretation of the rotational band structure of the acetylene molecule.

Tetratomic Linear Molecule

In order to compute the kinetic energy, the $f_{ia\lambda}$, and hence the $z_{ia\lambda}$, must be found explicitly by solving Eqs. (5), (6), (9) and (10). Written in scalar form, Eqs. (9) and (10) are:

$$\begin{aligned}&\Sigma_a m_a^{\frac{1}{2}}z_{\lambda ia}=0 \quad (i=x,\ y,\ z)\\ &\Sigma_a m_a^{\frac{1}{2}}z_{za}z_{\lambda xa}=0\\ &\Sigma_a m_a^{\frac{1}{2}}z_{za}z_{\lambda ya}=0,\end{aligned} \tag{11}$$

while Eq. (6), which is also invariant under a rotation of the axes, takes the form

$$\Sigma_a\Sigma_i z_{\lambda ia}z_{\mu ia}=A\,\delta_{\lambda\mu}. \tag{12}$$

The $3N-5=7$ linearly independent solutions of (11) can then always be chosen normalized and orthogonal so as to satisfy (12), in which A is conveniently taken to be the equilibrium moment of inertia, $\Sigma_a m_a z_{za}^2$. To find particular solutions, set $z_{\lambda xa}=z_{\lambda ya}=0$; the one remaining equation has three independent solutions: $z_{1za}=g_a^{(1)}$, $z_{2za}=g_a^{(2)}$, $z_{3za}=h_a$. Two of these are also solutions for $z_{\lambda za}=z_{\lambda ya}=0$ $(\lambda=4, 5)$, and for $z_{\lambda za}=z_{\lambda xa}=0$ $(\lambda=6, 7)$. Thus, q_1, q_2, q_3 describe the parallel vibrations, q_4 and q_6 one perpendicular mode, and q_5 and q_7, the other.

The potential energy must now be considered. On account of the rotational symmetry of the equilibrium configuration, *and* the choice of the $z_{\lambda ia}$, it must have the form:

$$2U_0=\Sigma_{\lambda,\mu}B_{\lambda\mu}q_\lambda q_\mu+b_{44}(q_4^2+q_5^2)+b_{55}(q_5^2+q_7^2)+2b_{45}(q_4q_5+q_6q_7),$$

where $\lambda, \mu=1, 2, 3$. Since there are four non-diagonal terms, there are four of Eqs. (5), and in order to satisfy these, it is necessary to form more general solutions of (11) without altering the character of the q's. This may be accomplished by taking separate orthonormal linear combinations of the solutions numbered 1, 2, 3, and of those numbered 4 and 5, which provides the four independent constants needed to diagonalize the potential energy. Because of the degeneracy of the perpendicular vibrations, the same combinations used for solutions 4 and 5 must be employed for solutions 6 and 7. The complete solution may therefore be written:

$$\begin{aligned}&z_{\lambda xa}=\alpha_{\lambda 1}g_a^{(1)}+\alpha_{\lambda 2}g_a^{(2)}+\alpha_{\lambda 3}h_a \quad (\lambda=1, 2, 3)\\ &z_{4xa}=z_{6ya}=\beta_{11}g_a^{(1)}+\beta_{12}g_a^{(2)}\\ &z_{5xa}=z_{7ya}=\beta_{21}g_a^{(1)}+\beta_{22}g_a^{(2)}.\end{aligned}$$

The Hamiltonian

The Hamiltonian kinetic energy, readily computed by the method of Wilson and Howard,[7]

[6] C. Eckart, reference 1, Eq. (25), p. 556. Also, E. B. Wilson, Jr., and J. B. Howard, J. Chem. Phys. **4**, 261 (1936), Eq. (3).

[7] E. B. Wilson and J. B. Howard, reference 6.

turns out to be

$$2AT=f^{-2}[M_x-\Lambda_x)^2+(M_y-\Lambda_y)^2]+\Sigma p_\lambda^2,$$

where p_λ is conjugate to q_λ, $\mathbf{M}$ $(=M_x\boldsymbol{\varepsilon}_x+M_y\boldsymbol{\varepsilon}_y+M_z\boldsymbol{\varepsilon}_z)$ is the total angular momentum about the center of mass, and

$$f=1+\alpha_{13}q_1+\alpha_{23}q_2+\alpha_{33}q_3.$$

The calculation also yields the result that

$$M_z-\Lambda_z=0.$$

The quantities Λ are identical (except for a normalization factor) with Wilson and Howard's p_x, p_y, p_z, and are given by

$$\Lambda_x=(1/A)\Sigma\mathfrak{X}_\lambda p_\lambda;\qquad \Lambda_y=(1/A)\Sigma\mathfrak{Y}_\lambda p_\lambda;$$
$$\Lambda_z=(1/A)\Sigma\mathfrak{Z}_\lambda p_\lambda,$$

in which

$$\mathfrak{X}_\lambda=\Sigma_\mu\Sigma_a(z_{\lambda za}z_{\mu ya}-z_{\lambda ya}z_{\mu za})q_\mu$$
$$\mathfrak{Y}_\lambda=\Sigma_\mu\Sigma_a(z_{\lambda xa}z_{\mu za}-z_{\lambda za}z_{\mu xa})q_\mu$$
$$\mathfrak{Z}_\lambda=\Sigma_\mu\Sigma_a(z_{\lambda ya}z_{\mu xa}-z_{\lambda xa}z_{\mu ya})q_\mu.$$

Finally, the relations of M_x and M_y to the momenta conjugate to θ, ϕ, and q_λ are:

$$M_x=-(1/s)P_\phi+(c/s)\Lambda_z$$
$$M_y=P_\theta.$$

It should be noted that the Λ's, which always appear in the Hamiltonian of a rotating vibrator, are not the same as the components of the vibrational or internal angular momentum. The latter are defined as $\Sigma\mathfrak{X}_\lambda\dot{q}_\lambda$, etc., rather than as $\Sigma\mathfrak{X}_\lambda p_\lambda$.

The calculation of the characteristic values of the Hamiltonian operator is entirely analagous to that performed by Weinberg and Eckart[8] for the triatomic linear molecule, so that only the important steps will be described here.

The perturbation calculation

The approximation,

$$f=1,$$

is equivalent to neglecting terms of third order and higher, while Casimir's condition ensures the absence of first-order terms. There remain only terms of zero and second order, and these are:

$$2AT_0=\Sigma p_\lambda^2$$
$$T_2=T-T_0.$$

If polar coordinates[9] are introduced,

$$q_4=\rho_1\cos\chi_1;\qquad q_5=\rho_2\cos\chi_2$$
$$q_6=\rho_1\sin\chi_1;\qquad q_7=\rho_2\sin\chi_2,$$

the zero-order wave functions are, in Dennison's[10] notation,

$$\psi_0=v(\theta,\phi)\psi^{V_1}(q_1)\psi^{V_2}(q_2)\psi^{V_3}(q_3)$$
$$\times R^{V_4l_1}(\rho_1)e^{\pm il_1\chi_1}R^{V_5l_2}(\rho_2)e^{\pm il_2\chi_2},$$

in which $l_1=V_4,\ V_4-2,\ \cdots\ 1$ or 0, etc. and $v(\theta,\phi)$ is an undetermined coefficient. This can also be written:

$$\psi_0=v(\theta,\phi)u_{ng}{}^N(q,\rho,\chi),$$

where N is an abbreviation for the quantum numbers V, n ranges over all the combinations l_1l_2, and g may have the values $++$, $+-$, etc. The zero-order energy,

$$W_0{}^N=\Sigma_i(V_i+\tfrac{1}{2})\hbar\omega_i+(V_4+1)\hbar\omega_4+(V_5+1)\hbar\omega_5,$$

is therefore of weight $\pi_n=(V_4+1)(V_5+1)$. In this and all following summations in this section, the index i has the range 1, 2, 3. Since the first-order energy corrections, W_1, due to the addition of cubic terms in the potential energy, are all zero, the degeneracy is unaltered to this approximation, and the correct zero order combinations for the second-order calculation are

$$\Sigma_n\Sigma_g v_{ng}u_{ng}.$$

If the operators T are defined by

$$T_{ng}{}^{n'g'}v=\int u^*{}_{n'g'}T_2v_{ng}u_{ng}dq_1\cdots dq_7,$$

the secular equations have the form:

$$\Sigma_n\Sigma_g T_{ng}{}^{n'g'}v_{ng}=W''v_{n'g'},$$

in which W'' is that part of the second-order energy correction, W_2, arising from T_2 alone. This "separability" of W_2 is possible only because the matrix elements of the first-order potential energy have the property:

$$(U_1)_{ng}{}^{mh}=0\qquad (mh\neq ng),$$

where mh has the same significance as ng but

[8] A. Weinberg and C. Eckart, J. Chem. Phys. **5**, 517 (1937).

[9] The operators must be transformed correspondingly: $p_4=\cos\chi_1p_\rho-\rho^{-1}\sin\chi_1p_\chi$, etc.; Λ_z becomes simply: $p_{\chi_1}+p_{\chi_2}$.

[10] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

refers to a wave-function for any state other than W_0^N. The kinetic energy operators themselves have the form:

$$T_{n\varrho}{}^{n'\varrho'} = T_{n\varrho}\delta_{n\varrho,\,n'\varrho'}$$

and are

$$T_{\pm\pm} = (1/2A)\{s^{-1}P_\theta s P_\theta + s^{-2}[P_\phi - \hbar c(\pm l_1 \pm l_2)]^2\} + C.$$

The characteristic values are immediately available:

$$W'' = (\hbar^2/2A)[J(J+1) - K^2] + C,$$

where $K = (\pm l_1 \pm l_2)$, $J = |K|, |K|+1, \cdots$. The first part is essentially the energy of a linear symmetric top, while the energy of interaction is

$$C = (\hbar^2/2A)\{(V_4+1) \times [\Sigma r_i^2(V_i+\tfrac{1}{2})(\omega_i/\omega_4 + \omega_4/\omega_i)] + (V_5+1)[\Sigma t_i^2(V_i+\tfrac{1}{2})(\omega_i/\omega_5 + \omega_5/\omega_i)] - 2\},$$

in which the integer 2 appears because there are two degenerate perpendicular vibrations, and

$$r_i = \alpha_{i1}\beta_{11} + \alpha_{i2}\beta_{12}$$
$$t_i = \alpha_{i1}\beta_{21} + \alpha_{i2}\beta_{22}.$$

This is analagous to Weinberg and Eckart's result for the triatomic case, and the generalization to an n atomic linear molecule is obvious.

For the symmetric molecule X_2Y_2, the following simplifications occur:

$$r_1 = 1; \quad r_2 = r_3 = 0$$
$$t_1 = 0; \quad t_2 = -(1-t_3^2)^{\frac{1}{2}}.$$

Thus, one constant, in addition to the normal frequencies, remains to be determined by the potential energy.

Anomalous Molecules

These are molecules possessing internal motions with amplitudes too large to be treated as normal vibrations, as, for example, the free internal rotation of an ethane-like molecule. Another example, to be discussed here, is a model of the ammonia molecule, in which it is supposed that the nitrogen atom, in an excited vibrational state, can surmount a relatively low potential barrier and vibrate between two extreme positions on opposite sides of the plane of the hydrogen atoms.

YX_3

The rigidly constrained configuration, YX_3, is taken to be a tetrahedron of variable height with the Y nucleus at the apex, on the z axis of a moving system of axes, while the X nuclei form an equilateral triangle parallel to the x–y plane. The anomalous coordinate, $\alpha'' = z$, is thus the z coordinate of the Y atom. The remaining coordinates are, as before, the three cartesian coordinates of the origin, three Eulerian angles, and five normal coordinates.

If the X nuclei, of mass m, are numbered 1, 2, 3 and the axes are the principal axes of the equilibrium configuration, the vectors $\mathbf{z}_a$ are:

$$\begin{aligned}
\mathbf{z}_1 &= -(S/2)\boldsymbol{\varepsilon}_x - (\sqrt{3}/6)S\boldsymbol{\varepsilon}_y - (M/3m)z\boldsymbol{\varepsilon}_z \\
\mathbf{z}_2 &= (S/2)\boldsymbol{\varepsilon}_x - (\sqrt{3}/6)S\boldsymbol{\varepsilon}_y - (M/3m)z\boldsymbol{\varepsilon}_z \\
\mathbf{z}_3 &= (\sqrt{3}/3)S\boldsymbol{\varepsilon}_y - (M/3m)z\boldsymbol{\varepsilon}_z \\
\mathbf{z}_4 &= z\boldsymbol{\varepsilon}_z,
\end{aligned}$$

where M is the mass of the Y nucleus, and S represents the side of the equilateral triangle. Note that the lengths of the $\mathbf{z}_a$ are not constant, as for a normal molecule, but vary with the time.

The position vectors for the elastically constrained motion are given by

$$\mathbf{r}_a = \mathbf{z}_a + m_a^{\frac{1}{2}}\boldsymbol{\delta}_a,$$

where $\boldsymbol{\delta}_a$, the mass-adjusted displacement from equilibrium, is defined as

$$\begin{aligned}
\boldsymbol{\delta}_a &= \Sigma_\lambda q_\lambda \mathbf{d}_{a\lambda} \\
&= \Sigma_j \Sigma_\lambda z_{\lambda ja} q_\lambda \boldsymbol{\varepsilon}_j.
\end{aligned}$$

Finally, the seven equations, $B_{p\lambda}{}^{(0)} = 0$, may be written:

$$\begin{aligned}
\Sigma m_a^{\frac{1}{2}}\boldsymbol{\delta}_a &= 0 \\
\Sigma m_a^{\frac{1}{2}}\mathbf{z}_a \times \boldsymbol{\delta}_a &= 0 \\
\boldsymbol{\delta}_4 \cdot \boldsymbol{\varepsilon}_z &= 0.
\end{aligned} \tag{13}$$

The seventh equation states that no normal vibration involves motion of the Y atom along the z axis, or that all $z_{\lambda z4} = 0$.

The potential energy,

$$U = U(q_1 \cdots q_5, z),$$

when expanded about the point $q_\lambda = 0$, $z = z$, takes the form:

$$U = U(z) + \Sigma_\lambda \Sigma_\mu b_{\lambda\mu}(z) q_\lambda q_\mu + \cdots.$$

This assumes that for $q_\lambda = 0$, the X atoms are in equilibrium for all values of z, which is, of course,

an approximation. The normal vibrations are given by the five orthonormal solutions of (13) which diagonalize the quadratic part of the potential energy. Three of these, ($\lambda=1, 2, 3$), are identical with the normal vibrations of three equal atoms at the corners of an equilateral triangle, the Y atom being unaffected. The coefficients describing the remaining double vibration, ($\lambda=4, 5$), are:

$$\begin{gathered} z_{4x\alpha}=z_{5y\alpha}=0 \\ z_{4y\alpha}=z_{5x\alpha}=-(1/3)(M/m)^{\frac{1}{2}}d \quad (\alpha\neq 4) \\ z_{4y4}=z_{5x4}=d \\ z_{4z1}=z_{4z2}=-\tfrac{1}{2}Kdz \\ z_{4z3}=Kdz \\ z_{5z1}=-z_{5z2}=-(\sqrt{3}/2)Kdz \\ z_{5z3}=0, \end{gathered}$$

where K is a constant, but d is a function of z determined by the requirement that the normalization factor be independent of z. What is sometimes referred to as the sixth "normal vibration," namely; the z motion of the Y atom, is determined by $U(z)$. Furthermore, since the amplitudes of some of the other vibrations depend on z, this variable enters the interaction terms of the kinetic energy in a rather complicated manner. If the experimental data warrants it, it would be interesting to investigate the contribution of such terms to the energy levels.

Hamiltonian kinetic energy

It is now possible to calculate the second-order terms in the Hamiltonian of our model with complete generality. The Lagrangian kinetic energy is:

$$2T=\Sigma m_\alpha(\dot{\mathbf{R}}+\dot{\mathbf{r}}_\alpha)^2$$

and

$$\dot{\mathbf{r}}_\alpha=\boldsymbol{\omega}\times\mathbf{r}_\alpha+\dot{\mathbf{z}}_\alpha+m_\alpha^{-\frac{1}{2}}\dot{\boldsymbol{\delta}}_\alpha.$$

Taking account of Eqs. (13) and their time derivatives, and neglecting terms quadratic in q_λ, since these give rise to terms of third or higher order, one gets:

$$\begin{aligned} 2T=\Sigma_i\Sigma_j I_{ij}\omega_i\omega_j+2\omega_x(\Sigma\mathfrak{X}_\lambda\dot{q}_\lambda+R_1\dot{z}) \\ +2\omega_y(\Sigma\mathfrak{Y}_\lambda\dot{q}_\lambda+R_2\dot{z})+2\omega_z\Sigma\mathfrak{Z}_\lambda\dot{q}_\lambda \\ +\mu M\dot{z}^2+A\Sigma\dot{q}_\lambda^2, \end{aligned}$$

in which the I_{ij} are the instantaneous moments and products of inertia, and

$$\begin{gathered} \mu=(M/3m)+1 \\ R_1=2\mu M^{\frac{1}{2}}dq_4 \\ R_2=-2\mu M^{\frac{1}{2}}dq_5. \end{gathered}$$

Notice that the zero-order term in z, which is separable, involves μM rather than M.

The Hamiltonian kinetic energy takes the form:

$$2T=\Sigma_i(M_i-\Lambda_i)^2/I_i^\circ+P_z^2/M\mu+(1/A)\Sigma p_\lambda^2,$$

where I° is an equilibrium moment of inertia, and depends on z. As before, $M_i=\partial T/\partial\omega_i$ and $P_z=\partial T/\partial\dot{z}$ but the Λ_i are now defined by

$$\begin{gathered} \Lambda_x=(1/A)\Sigma\mathfrak{X}_\lambda p_\lambda+(R_1/M\mu)P_z \\ \Lambda_y=(1/A)\Sigma\mathfrak{Y}_\lambda p_\lambda+(R_2/M\mu)P_z \\ \Lambda_z=(1/A)\Sigma\mathfrak{Z}_\lambda p_\lambda. \end{gathered}$$

Ethane

This molecule has been studied in detail by Howard,[11] and it will be sufficient to mention that the equations by which he removes the degrees of freedom corresponding to "incipient translations, over-all rotations, and internal rotation" are the seven equations, $B_{p\lambda}^{(0)}=0$, appropriate to his choice of the seven rigid constraint variables. Six of these variables are identical with those chosen here for normal molecules, as are the corresponding six equations (our Eqs. (9) and (10)); the seventh coordinate, which describes the internal motion, is taken to be the angle between the two methyl groups, considered as rotating relative to each other about a common axis, (the z axis of the moving system).

The seventh equation turns out to be:

$$\Sigma_\alpha m_\alpha^{\frac{1}{2}}\mathbf{z}_\alpha\times\mathbf{d}_{\alpha\lambda}\cdot\boldsymbol{\epsilon}_z=0,$$

where the summation extends over the atoms of one methyl group only. This means that, in first approximation, the z component of the angular momentum of each methyl group vanishes separately.

Acknowledgment

I take pleasure in acknowledging the invaluable assistance of Professor Carl Eckart, who also suggested the investigation.

[11] J. B. Howard, J. Chem. Phys. **5**, 442 (1937); **5**, 451 (1937).

The Reactions of Methyl Radicals with Deuterium, Ethane, Neopentane, Butane and Isobutane

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Methyl radicals produced by photodecomposition of mercury dimethyl have been allowed to react with deuterium, ethane, neopentane, butane and isobutane in the temperature range 100–300°C. The kinetics of the processes have been ascertained. Ethane production was found to be bimolecular, methane production between first and second order with respect to methyl radical concentrations. From the rate of methane formation as a function of temperature the following activation energies for the reaction of methyl radicals were obtained: with deuterium 8.1, ethane and neopentane 8.3, butane 5.5 and isobutane 4.2 kcal. These values are based on an assumed activation energy $E=0$ for ethane formation. The data of Kistiakowsky on the heats of hydrogenation of the substituted ethylenes suggest that the bond energies of primary, secondary and tertiary C−H bonds are measurably different. The differences being approximately 2.5 kcal. between primary and secondary and 4.0 kcal. between primary and tertiary C−H bonds in saturated aliphatic hydrocarbons. These differences correspond approximately to the differences in the activation energies noted above. It is proposed that such differences be accepted as a second approximation to the prevailing assumption of equal energies for such C−H bonds.

THIS research represents an attempt to determine the activation energies of the reactions between methyl radicals and deuterium, ethane, neopentane, butane and isobutane and is a continuation of the work with Cunningham[1] on the reaction between methyl radicals and hydrogen. It also gives some indication of the stability of the larger radicals. The methyl radicals were produced by the photolysis of mercury dimethyl in the unfiltered radiation of the "hot" mercury-in-quartz arc.

EXPERIMENTAL DETAILS

Mercury dimethyl vapor at the vapor pressure of the liquid at room temperature (~40 mm) was admixed with ~200 mm of the gas to be investigated, by means of apparatus similar to that employed by Cunningham, a quartz reaction vessel, which was completely sealed off from the system during the photolysis, being employed. This avoided condensation of liquid mercury dimethyl in the cooler zones of the reaction vessel when experiments were conducted at elevated temperatures and avoided difficulties due to the solubility of mercury dimethyl in stopcock grease and Picein.

The illumination was furnished by a vertical mercury-in-quartz arc operated "hot" either at 3.5 amp. and 50 volts or 4.0 amp. and 60 volts. Cunningham has shown that no measurable resonance radiation enters the reaction system under these conditions. The arc in the later experiments was placed at a fixed distance of 10 cm from the furnace in which the reaction vessel was placed and was started by a high tension discharge. In the earlier experiments (1–29) the arc was placed close to the furnace and started by tipping. This did not give very reproducible results. A frame was employed by means of which two copper gauze screens, superficially oxidized, could be interposed between the arc and reaction vessel, in order to vary the light intensity. A relative calibration of the intensities with the screens in and out was obtained by the use of a Moll large surface thermopile and a Leeds & Northrup high sensitivity galvanometer.

The furnace, about twice the length of the reaction vessel, was made of block aluminum, with walls 2.5 cm in thickness. An aperture, the length of the reaction vessel and 1.25 cm wide, was cut in its side. The aperture was covered with a quartz window and the furnace wound so that no wire crossed the window. The maximum temperature variation inside the furnace at 300°C was 10°C.

Materials

The mercury dimethyl used has been described by Cunningham.[1] The deuterium, prepared by the electrolysis of a 10 percent solution

[1] J. P. Cunningham and H. S. Taylor, J. Chem. Phys. **6**, 359 (1938).

of potassium deuteroxide in heavy water, was passed over a hot platinum spiral and dried. The ethane was prepared by the hydrogenation of fractionated tank ethylene over active copper at 130°C and purified by repeated freezing and evacuation of the excess hydrogen. Normal butane and isobutane were obtained by the fractionation, by condensation and evacuation, of commercial products of high grade. The neopentane was kindly given to us by Dean F. C. Whitmore of Pennsylvania State College. The gases were employed in a constant ratio, ~40 mm of mercury dimethyl vapor and 200 mm of the added gas.

Procedure and analysis

The experimental procedure in our work with mercury dimethyl-deuterium mixtures followed closely that developed by Cunningham. In the case of ethane, normal butane, isobutane and neopentane the gas was measured in an auxiliary burette and frozen into the reaction vessel by means of liquid air.

After reaction, with deuterium as the admixed gas, the gases noncondensable in liquid air were removed, by repeated freezing, pumping and melting. The fraction so obtained was assumed to be deuterium and methane, and was analyzed by burning the former over copper oxide at 280°C. The remaining gas was assumed to be methane.

The residue from the photolysis was next condensed in solid carbon-dioxide-toluene mixture and the residual gas pumped off and measured. Since one-half of the methane plus this residual gas, assumed to be ethane, was very closely equal to the mercury dimethyl decomposed, it is reasonable to suppose that the gas was ethane, confirming Cunningham's results.

In the ethane-mercury dimethyl experiments only methane and the residual mercury dimethyl were determined.

In the butane, isobutane and neopentane experiments, methane and hydrogen were determined as in the deuterium experiments. Next, a fraction resulting from evacuation at −135 to −140°C was taken. No unsaturates were found in this fraction on analysis and so the fraction was assumed to be ethane. The gases volatile at −78°C were next removed and the residue recorded as mercury dimethyl. With some of these gas mixtures it was demonstrated that higher hydrocarbons were present in the mercury dimethyl. Since the emphasis in this research is on the rate of methane formation, no special importance attaches to the exact determination of residual mercury dimethyl, which was largely determined for purposes of control of the experimental procedure.

Experimental Results

Mercury dimethyl-deuterium mixtures

The experiments Nos. 1–28 were performed in a vessel previously used by Cunningham and cleaned between experiments by nitric acid and by chromic acid cleaning solution. It was found that the methane production was not very reproducible and a slight film formed on the vessel walls. In all the later experiments the vessel was cleaned in nitric acid, rinsed with water and then heated to glowing in an oxygen-gas flame. This gave a clean surface and more reproducible results.

The data for Exp. 30–45 are presented in Table I, for two light intensities (a) and (b) using two quartz vessels and the new cleaning technique. The two light intensities employed are in

Table I. *Photochemical decomposition of mercury dimethyl in presence of deuterium using a new vessel and "torching out."*

No.	T°K	$k_{CH_4}\times10^3$	$k_{C_2H_6}\times10^3$	$k_{Hg(CH_3)_2}\times10^3$
a. At normal light intensity				
34	366	2.345	20.1	21.9
40	464	31.7	34.2	49.8
41	464	24.8	32.6	49.8
30	464	24.6	28.9	40.1
32	539	80.4	30.4	75.4
b. At low light intensity				
35	366	0.727	2.81	3.21
31	464	5.56	3.67	6.63
33	539	27.6	3.33	18.6
c. At normal light intensity with packing				
42	464	14.1	24.8	29.9
43	464	19.5	26.4	33.6
45	464	19.6	28.1	38.0
44	538	81.0	28.0	73.4

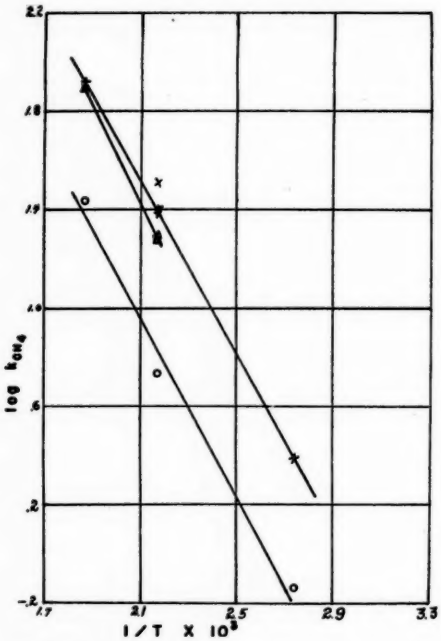

FIG. 1. Methane formation in mercury dimethyl-deuterium mixtures, normal light intensity, crosses; reduced light intensity, circles; packed vessel, triangles.

the ratio of 1 : 0.15. The k's are the rates of formation or disappearance of the indicated substances in cc at NTP per minute. Both sets of data give straight line relationships for log $k_{CH_4}-1/T$ closely paralleling each other. (Fig. 1, crosses and circles.)

A study of the ratios of the rates of methane production at the two intensities (Table II), shows that the order of the methane production with respect to light intensity increases with increasing temperature. A comparison of the data for ethane shows that ethane has a higher order of dependence on light intensity than methane and that this order increases slightly with increasing temperature. This is significant with regard to the mechanism of methane production and will be treated in detail later.

In Exp. 42–45, Table I, the reaction vessel was packed with quartz tubing, six mm external diameter, one mm wall thickness and approximately the length of the containing vessel. The results show that, at 200°C, packing does not affect the ethane production but decreases the methane production and mercury dimethyl decomposition. However, at 275°C the packing apparently has no effect on any of the reactions. These results can be explained by assuming that, at 200°C, a radical or atom which can effect mercury dimethyl decomposition is removed by the surface when it is increased by packing but that, at 300°C, the reaction between the atom or radical and mercury dimethyl is so rapid that the increased surface has no effect. The observation that the decomposition at 300°C is as fast in the packed as in the unpacked vessel indicates that the quartz packing does not materially change the amount of light absorbed by the mercury dimethyl. A comparison of runs 42, 43 and 45 indicates the reproducibility of the results. The activation energy (Fig. 1, triangles) for the methane producing process appears to be slightly higher in the packed vessel.

Mercury dimethyl-ethane mixtures

The results with ethane are summarized in Table III. The plot of log $k_{CH_4}-1/T$ gives a satisfactory straight line (Fig. 2). The amount of ethane formed or disappearing could not be measured in presence of the excess ethane.

Mercury dimethyl-neopentane mixtures

The results are recorded in Table IV. Again, the log $k_{CH_4}-1/T$ plot gave a straight line lying parallel to but above the curve with admixed ethane (Fig. 2). The difference in the rates of formation of methane in the cases of ethane and neopentane at a given temperature can be accounted for by a reasonable difference in the collision diameters of the two hydrocarbon molecules.

In no case was any unsaturate found in the reaction products.

Mercury dimethyl-butane mixtures

The results are recorded in Table V. The log $k_{CH_4}-1/T$ plot gives a satisfactory straight line (Fig. 3). The product reported as ethane

TABLE II. *The effect of light intensity on the yields of methane and ethane.*

T°C	$\frac{k_{CH_4}}{k'_{CH_4}*}$	$\frac{k_{C_2H_6}}{k'_{C_2H_6}*}$
93	3.23	7.15
191	4.43	7.9
266	5.56	9.1

* The prime indicates the light intensity has been reduced to 1/67. its normal value.

was that pumped off at −135 to −140°C. Unsaturates were shown to be absent. Among the products was a hydrocarbon with a vapor pressure in the same range as that of mercury dimethyl.

In a special effort to detect unsaturates the last recorded experiment was made with reduced light intensity at a temperature of 130°C with excess mercury dimethyl and for a period of 60 hours. It was thought that, by minimizing the stationary state concentration of free radicals, conditions might favor the breakdown of the radical $CH_3 \cdot CH_2 \cdot CH \cdot CH_3$ to a smaller radical and an unsaturate. Analysis revealed no more than a trace of unsaturated hydrocarbon. It was also found, in a single experiment, that the ratio of methane to ethane formed did not vary at the two light intensities, which would indicate, if this phenomenon subsequently were shown to be general, that the reactions of formation were of the same order with respect to free radical concentration. For the present we are ignoring this result since, in the experiment in question, the mercury dimethyl concentration was abnormally high and could have yielded ethane by interaction with methyl, unimolecularly with respect to this latter.

Mercury dimethyl-isobutane mixtures

The results, presented in Table VI again show a satisfactory straight line for $\log k_{CH_4} - 1/T$ (Fig. 3). Tests showed unsaturates to be absent from the gaseous products. The residue contained hydrocarbons with vapor pressures similar to that of mercury dimethyl.

Interpretation of Results

Mercury dimethyl and deuterium

Any interpretation of the results must explain the following facts from the present work and that of Cunningham. (1) The formation of ethane in the absence and presence of hydrogen or deuterium remains unchanged. (2) The formation of methane increases rapidly with temperature, and this increase is paralleled by an increase in the rate of decomposition of mercury dimethyl. (3) The formation of ethane shows a first-order dependence on light intensity while the methane production shows an order between the one-half and the first power, increasing toward first power with increasing temperature. (4) Packing the vessel at 200°C cuts down the amount of methane formed but does not affect the ethane production. (5) The mercury dimethyl decomposes photochemically into free methyls. (6) The rate of mercury dimethyl decomposition is independent of its concentration.

Table III. *Photolysis of 40 mm mercury dimethyl and 200 mm ethane.*

$T°K=$	303	425	464	514	562
$k_{CH_4} \times 10^3$	0	3.28	8.21	19.11	35.2
$k_{Hg(CH_3)_2} \times 10^3$	14	28	29.2	34.8	43.9

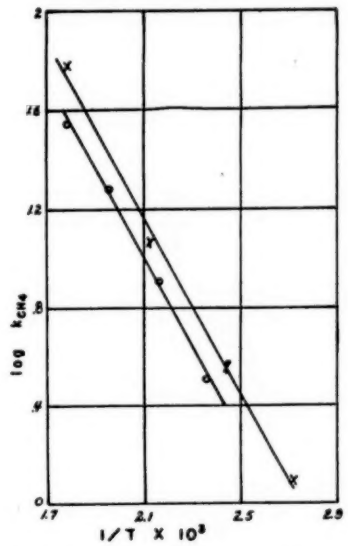

Fig. 2. Methane formation in mercury dimethyl mixtures with ethane (circles) and neopentane (crosses).

A mechanism meeting all these requirements is:

$$Hg(CH_3)_2 + h\nu = HgCH_3 + CH_3 \qquad (I \cdot k_1)$$
$$HgCH_3 = Hg + CH_3$$

$$CH_3 + CH_3 = C_2H_6 \qquad (k_5)$$

$$CH_3 + CH_3 = CH_4 + CH_2 \qquad (k_6)$$

$$CH_3 + D_2 = CH_3D + D \qquad (k_2)$$

$$CH_2 + D_2 = CH_2D + D \qquad (k_4)$$

$$D + Hg(CH_3)_2 = CH_3D + CH_3 + Hg. \qquad (k_3)$$

From the stationary state concentrations for the respective radicals one obtains the rate equation

for the formation of methane as:

$$\frac{d[CH_4]}{dt}=k_{CH_4}=2k_6[CH_3]^2+2k_2[CH_3][D_2]$$
$$=2k_6\frac{k_1I_{abs}}{k_5}+2k_2\left(\frac{k_1I_{abs}}{k_5}\right)^{\frac{1}{2}}[D_2].$$

The determination of the activation energy for methyl and hydrogen rests on the assumption that k_1, I_{abs} and k_5 are constants independent of temperature. Consideration of the data of Linnet and Thompson,[2] of Cunningham and those of Terenin[3] on the absorption spectra confirm this assumption as to k_1 and I. With respect to k_5 we assume independence of temperature on the basis of data previously discussed.[4] Davis, Jahn and Burton[5] conclude that methyls do not readily recombine to give ethane. Allen and Bawn[6] concluded that more than ten collisions were necessary. Our investigation on the influence of light intensity constitutes satisfactory evidence for the bimolecular formation of ethane, with the packing experiments tending also to prove this.

The factor of intensity between 0.5 and 1.0 in the case of methane formation demands in part a bimolecular process of methane formation, one such being given as k_6. The reaction $CH_3+H=CH_4$ we have discounted because, if important, the accelerating effect of added hydrogen on the dimethyl decomposition is difficult to explain. This increased decomposition parallels the methane formation. Decreased methane formation in packed vessels points to disappearance of hydrogen atoms on the wall rather than by attack on mercury dimethyl. The absence of such packing effect at 300° we account for by increased reactivity of atomic hydrogen with mercury dimethyl. The reaction of methylene with hydrogen (k_4) is indicated by the data of Rosenblum[7] and helps to account for the observed absence of unsaturates.

The slopes of the lines (crosses and circles), log k_{CH_4} *vs.* $1/T$ in Fig. 1 correspond to an activation energy of 8.1 kcal. with both light intensities employed. Within the experimental error the influence of the disproportionation reaction on the temperature coefficient of CH_3+H_2 is negligible at the light intensities employed. Packing (triangles) changes the slope to higher values.

If one deducted from the observed value, 8.1 kcal., for the activation energy of methyl and deuterium, 1.76 kcal., the zero-point energy difference between hydrogen and deuterium, this would yield for the activation energy of methyl plus hydrogen, a value of 6.34 kcal., which is somewhat below the values indicated by recent work from this laboratory. We are unable to correct this for the differences in zero-point energies of the activated states. If the energy of activation of ethane formation is not zero, one-half of this activation energy would have to be added to the value given for the reaction of methyl with deuterium.

TABLE IV. *Photolysis of 40 mm mercury dimethyl and 200 mm neopentane.*

$T°K=$	369	411	473	562
$k_{CH_4}\times10^3$	1.26	3.58	11.70	60.5

Mercury dimethyl and the hydrocarbons

The following mechanism is suggested for these interactions:

$$Hg(CH_3)_2+h\nu=2CH_3+Hg \qquad I_{abs}$$
$$CH_3+RH=CH_4+R \qquad k_1$$
$$R+CH_3=RCH_3 \qquad k_2$$
$$CH_3+CH_3=C_2H_6. \qquad k_3$$

Reactions of the type, $CH_3+Hg(CH_3)_2=C_2H_6+CH_3+Hg$, probably also occur as indicated by

TABLE V. *Photolysis of 40 mm mercury dimethyl and 200 mm butane.*

$T°K=$	369	404	474	561	398*
$k_{CH_4}\times10^3=$	4.72	10.02	28.1	59.6	1.67*
$k_{C_2H_6}\times10^3=$	12.6	5.58	6.21	7.05	1.00*

* Experiment with light intensity 0.15 of the normal value.

[2] J. W. Linnett and H. W. Thompson, Trans. Faraday Soc. **31**, 501 (1937).
[3] A. Terenin and N. Prileshajeva, Acta Physicochem. U. S. S. R. **1**, 762 (1935).
[4] H. S. Taylor and C. Rosenblum, J. Chem. Phys. **6**, 119 (1938).
[5] T. W. Davis, F. P. Jahn and M. Burton, J. Am. Chem. Soc. **60**, 10 (1938). See also C. J. M. Fletcher and G. K. Rollefson, *ibid.* **58**, 2135 (1936); D. V. Sickman, J. Chem. Phys. **4**, 297 (1936).
[6] Allen and Bawn, Trans. Faraday Soc. **34**, 463 (1928).
[7] C. Rosenblum, J. Am. Chem. Soc. **60**, 2819 (1938).

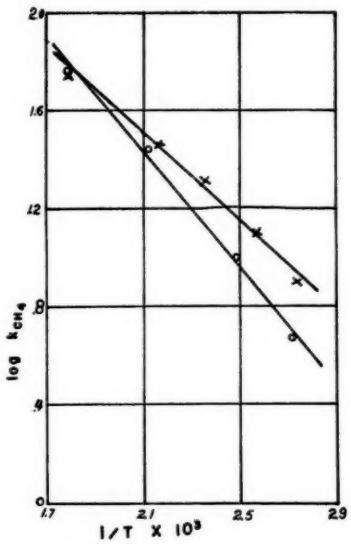

FIG. 3. Methane formation in mercury dimethyl mixtures with butane (circles) and isobutane (crosses).

Cunningham's results on the photodecomposition of mercury dimethyl in absence of hydrogen or added gas. Since, however, a methyl radical is produced as well as consumed no change in the methyl concentration results. The above reaction sequence yields for the rate of methane formation:

$$\frac{d[CH_4]}{dt}=k_1\frac{-2k_1[RH]+(4k_1[RH]^2+8k_3I_{abs})^{\frac{1}{2}}}{2k_3}$$

$$\times[RH]=k_1[RH]\cdot A.$$

When ethane is the principal product, the quadratic expression designated as A will be sensibly constant. The curve log k_{CH_4} *vs.* $1/T$ will be a straight line and its slope will give the true activation energy for k_1. The lower range of temperature here studied appears to be in this region. An exponential variation of A which would yield the same result is very unlikely.

When ethane formation is unimportant the rate determining step would be that of methyl radical formation. The log k *vs.* $1/T$ curve would bend toward the temperature axis and the same rate of methane formation with all hydrocarbons would be approached. This condition appears in our high temperature range. The rate expression for this becomes $d[CH_4]/dt=I_{abs}$. At still higher temperatures probably in the range 500–600°C, the radicals R tend to decompose to give methyl radicals. This would again change the kinetic expression but does not concern us, since the thermal instability of mercury dimethyl restricts us to temperatures below 300°C. For determination of activation energies of interaction of methyl with the hydrocarbons it is obvious that these come from the measurements in the low temperature range. Our data in Fig. 3 show some curvature, but we believe the accuracy of the data is not such as would warrant anything other than the straight line approximation.

The activation energies of methyl and the hydrocarbons

From the slopes of the straight lines in Figs. 2 and 3, the activation energies deduced are: for ethane and neopentane, 8.3 kcal., for butane, 5.5 kcal. and for isobutane, 4.2 kcal.

That the activation energies for ethane and neopentane are the same indicates that the removal of primary hydrogens from hydrocarbons is, energetically, independent of the hydrocarbon. The ratio of 1.3 for the absolute rates in the two cases under similar conditions can be accounted for by the relative sizes of the two hydrocarbon molecules. The lower activation energies with butane and isobutane we ascribe to the greater reactivity of secondary and tertiary hydrogens. The value found for butane will be somewhat higher than the true value for secondary hydrogen since, at each temperature, some primary hydrogen may be reacting. The statistical factor of six primary to four secondary hydrogens favors the reaction of primary hydrogen but this factor does not change with temperature and should not therefore affect the activation energy. In the case of isobutane, with a large statistical factor of nine primary to one tertiary, conditions might be expected to favor primary hydrogen reaction but the low activation energy found, 4.2 kcal., indicates large tertiary hydrogen reaction, favored by the larger spread

TABLE VI. *Photolysis of 40 mm mercury dimethyl and 200 mm isobutane.*

$T°K=$	366	391	425	464	562
$k_{CH_4}\times10^3=$	8.04	12.7	20.6	29.6	56.3
$k_{C_2H_6}\times10^3=$		9.54	10.5	5.95	3.83

in energy $(8.3-4.2)=4.1$ kcal. as ΔE in the expression $e^{-\Delta E/RT}$ for the ratio of rates in the two cases of ethane and isobutane.

The activation energy differences here found of 2.8 and 4.1 kcal. between primary and secondary and primary and tertiary reactions compare favorably with the predictions of Rice,[8] 1.2 and 4.0 kcal. based upon the decomposition of hydrocarbon vapors, an analysis of the products and an interpretation of these in terms of assumed activation energies for the various intermediate steps. Our values therefore are contributory evidence in support of the chain mechanism of decomposition of saturated hydrocarbons, and supply reliable data for the activation energies of typical radical-molecule reactions.

We believe that the differences in activation energies here under discussion are closely related to the bond energies in question. We are aware of the dangers attending such an identification of one with the other but we are confirmed in our belief by the data of Kistiakowsky and his co-workers[9] on the heats of hydrogenation of the substituted ethylenes. Monosubstituted ethylenes on hydrogenation change a double bond to a single C−C bond and form one primary and one secondary C−H bond. With 1,1 disubstituted ethylenes one primary and one tertiary C−H bond are formed. Other types of substitution give other combinations. If the Harvard data be analyzed on this basis, it is found that as many as seven independent thermal measurements for the energy difference, primary-secondary, yield the value 2.4 ± 0.25 kcal. and, for the primary-tertiary difference, three measurements yield 4.4 kcal. We believe this cumulative evidence warrants a confident modification of the first approximation in the estimates of C−H bond energies in hydrocarbons which assigns them all an equal value. We suggest, as a second approximation, bond energy differences of 2.5 and 4 kcal. between primary and secondary and primary and tertiary C−H bonds in saturated hydrocarbons. We are exploring further the consequences of these assumptions.

[8] F. O. and K. K. Rice, *The Aliphatic Free Radicals* (Johns Hopkins Univ. Press, 1935).

[9] G. B. Kistiakowsky *et al.*, J. Am. Chem. Soc. **58**, 137 (1936); **59**, 831 (1937); **60**, 440 (1938).

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Depolarization Measurements on Raman Lines by an Easy, Accurate Method

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The depolarization factors of Raman lines are determined by a method in which a Polaroid disk, so oriented that it passes light whose electric vector is horizontal, is placed between the Raman tube and the lens which condenses the scattered light on the slit of the spectrograph. Two exposures of equal duration are made, one with the arc below, the other with it at the side, of the horizontal Raman tube. The ratio of the intensities in the two exposures (depolarization factor) is determined by comparison with the lines of seven argon spectra produced by argon light of known intensity ratios. Important advantages of the method are the comparatively short exposure times and the elimination of errors due to the polarization characteristics of the spectrograph. Results for the depolarization factors of Raman lines obtained from a mixture of benzene and carbon tetrachloride are given and comparison with previous data for these compounds is made.

ALTHOUGH information regarding the depolarization factors of Raman lines is of the greatest importance in assigning the frequencies to particular modes of vibration within the molecule, comparatively few data have been reported because of the difficulty and expense

connected with the methods previously used. Recently Edsall and Wilson[1] have described two arrangements which represent significant steps in the direction of making such measurements more universal in the Raman spectra field.

Discussion of the Edsall-Wilson Arrangements

In the first of these, light from four vertical mercury lamps, backed by parabolic reflectors, was passed through a cylinder of Polaroid so oriented that it transmitted light whose electric vector was parallel to the axis of the vertical Raman tube. A second exposure was made without the Polaroid and with the intensity of illumination reduced to the extent necessary to give the depolarized lines equal intensities in the two exposures. Lines which had nearly the same intensity in the two exposures were designated by *D* (depolarized) while lines whose intensities were appreciably different were designated by *P* (polarized). The method is an ingenious one for the qualitative distinction between polarized and depolarized lines, which is the purpose the authors had in mind. However, the considerations given below indicate that, from a quantitative point of view, the values of the *depolarization factors* (subsequently referred to as ρ) obtained by such a method would be too large.

Consider a *completely* polarized line: During the first exposure the electric vector is parallel to the axis of the Raman tube, hence no light will be scattered along the axis of the tube. In the second exposure, since polarized light is not employed, there will be components of the electric vector both perpendicular and parallel to the axis of the Raman tube. The component parallel to the axis will, as before, result in no scattering, but the perpendicular component will give scattering along the axis. Dividing the intensity of the line in the first exposure by its intensity in the second exposure, one obtains a value of zero for ρ, as is to be expected.

If, however, the line is partially depolarized, as practically all Raman lines are, it appears that an erroneous value of ρ would result. For, in reducing the intensity of all the lines on the plate to make the highly depolarized lines have the same intensity in the two exposures, the denominators of the depolarization ratios are made too small and consequently the values of ρ will be too large for all the lines on the plate. The only exception is the *completely* polarized line discussed above.

These points may be clarified by a consideration of Table I. Imagine three Raman lines, each with an intensity of 10, and having values of ρ equal to 0.86, 0.50 and 0.02, respectively. The upper part of the table gives the relative intensities that would have been obtained if the incident radiation had been polarized. The lower part of the table gives the relative intensities that would be obtained by the method of Edsall and Wilson, the corresponding values of ρ, and the errors in ρ.

For determining quantitative values of ρ, the method would be more exact if the intensity of the highly depolarized line in the second exposure had been made 7/6 as strong as in the first exposure. This would increase the intensities of the other two hypothetical lines by the same amount and the apparent values for ρ (Cf.

Table I. *Comparison of the values of ρ for three hypothetical Raman lines of equal intensity obtained by use of polarized light and by the method of Edsall and Wilson.*

Method	Incident light	Intensity of: Highly depolarized line	Partially depolarized line	Highly polarized line
Polarized incident light	Electric vector parallel to axis of Raman tube	4.6	3.3	0.2
	Electric vector perpendicular to axis of Raman tube	5.4	6.6	9.8
	True values of ρ	0.86	0.50	0.02
Edsall and Wilson	Electric vector parallel to axis of Raman tube	4.6	3.3	0.2
	Not polarized and intensity reduced	4.6	4.6	4.6
	Apparent values of ρ	1.00	0.72	0.04
	Errors in ρ values	0.14	0.22	0.02

[1] J. T. Edsall and E. B. Wilson, Jr., J. Chem. Phys. **6**, 124–127 (1938).

Table I) would then be 0.86, 0.61 and 0.04 with corresponding errors of 0.00, 0.11 and 0.02, rather than 0.14, 0.22 and 0.02, as before.

Another possibility would be to adjust the intensity so that the ρ value of some other line, e.g. one for which $\rho=0.5$, was correct. The result of this procedure, however, would be to make the ρ values for the highly depolarized lines too small.

Thus, in view of the foregoing discussion, it must be concluded that, as long as polarized light is used during one exposure and unpolarized light during the other, it is impossible to obtain quantitative values of ρ.

From the quantitative point of view, the arrangement would be vastly improved if during the second exposure a cylinder of Polaroid, constructed in such a manner that it transmitted only light whose electric vector was perpendicular to the axis of the Raman tube, had been employed. This would eliminate the troublesome parallel component and would also make the absorption of light by the Polaroid the same in the two exposures.

In the second arrangement used by Edsall and Wilson, light from a mercury arc was passed through a filter solution contained in a cylindrical glass tube which concentrated the light in a nearly parallel beam, through a plane sheet of Polaroid, along the axis of the Raman tube. Two exposures of equal duration were made, one with the Polaroid in a position to transmit light whose electric vector was parallel to the axis of the Raman tube, the second with the Polaroid rotated through an angle of 90°. Again, the intensity of illumination was reduced during the second exposure to make the strongly depolarized lines have the same intensity as in the first exposure. This arrangement would be satisfactory for quantitative purposes if the intensity during the second exposure were not reduced and if some method of correcting for the polarization characteristics of the spectrograph were employed. A major disadvantage, however, is that exposure times of the order of 24 hours were required for each of the two exposures, even with a fast spectrograph of aperture ratio $f:3$.

The present authors began preliminary experiments[2] with the use of Polaroid in November 1937, but were able to make only qualitative measurements at that time. Experimentation was resumed a year later and a method, similar in some respects to the second arrangement of Edsall and Wilson, has been developed. This method permits quantitative values of ρ to be determined with relatively short exposure times and with elimination of errors due to selective reflection of the polarized light in the spectrograph.

TABLE II. *Comparison of intensities of three hypothetical Raman lines with mercury arc and Polaroid in various positions.*

	Mercury arc	Polaroid set so that transmitted electric vector is:	Intensity of: Highly depolarized line	Partially depolarized line	Highly polarized line
A	Side	Horizontal	4.4	3.3	0.2
		Vertical	5.6	6.6	9.8
B	Below	Vertical	4.4	3.3	0.2
		Horizontal	5.6	6.6	9.8
C	Side	Horizontal	4.4	3.3	0.2
	Below	Horizontal	5.6	6.6	9.8

Experimental Procedure

Light from a cylindrical mercury vapor lamp[3] is passed through a test tube (21 mm in diameter) which contains the excellent filter solution used by Edsall and Wilson, and is concentrated in a nearly parallel beam along the axis of the horizontal Raman tube. The distance from the center of the filter tube to the center of the Raman tube is 25 mm and is kept constant by collars of wood which slip over the tubes. The mercury arc is adjusted so that the distance from its center to the center of the filter tube is 25 mm. Accuracy of adjustment is tested by holding a piece of thin white cardboard at the edge of the Raman tube opposite the light source. When the mercury arc, filter tube, and Raman tube are properly aligned, a symmetrical light strip, bordered by dark lines, appears on the cardboard. The cardboard is then replaced by a plane mirror in order to reflect the incident beam back upon itself and thus to increase the intensity of illumination.

[2] Forrest F. Cleveland and M. J. Murray, Phys. Rev. **53**, 330 (1938).

[3] Forrest F. Cleveland and M. J. Murray, Am. Phys. Teacher **5**, 270–272 (1937).

The scattered light is intercepted approximately 30 cm in front of the Raman tube by a Polaroid disk so oriented that it passes that component of the light whose electric vector is horizontal. Two exposures of equal duration are made, one with the mercury arc below, the other with it at the side, of the Raman tube. The current through the arc is carefully maintained at a constant value during the two exposures. The width of the slit is set at 0.17 mm. The film used was Agfa Super Plenachrome Press.

The method used for comparing the intensities of a given line in the two exposures is as follows: Seven argon spectra are photographed upon the same film with the intensities of the incident light varying in the ratios of 7 : 6 : 5 : 4 : 3 : 2 : 1, the exposure time for each being three hours, the same as that for the polarization film above. This variation in intensity is obtained by adjusting the perpendicular distance of an argon lamp (2 w, 110 v, a.c.) from a plane of white cardboard, placed in front of the one-hole stopper which normally holds one end of the Raman tube.

The stronger of the pair of lines on the polarization film is now matched with one of the lines in the same wave-length region on the most intense argon spectrum. The weaker of the Raman pair is then matched with the *same* argon line on one of the less intense argon spectra. The value of ρ is then given by the ratio of the two intensities. Thus, if the weaker of the Raman pair matches the line on the least intense argon spectrum, the value of ρ would be 1/7. If it matches the line on the next to the strongest argon spectrum, ρ would be 6/7, the theoretical maximum.

Discussion of Method

The ratio of the intensity of the Raman line in the second exposure (arc at the side) to that in the first exposure (arc below) gives the depolarization factor of the line. This may be made clear by reference to Table II. Imagine three lines, each of intensity 10, having ρ values of 0.86, 0.50 and 0.02, respectively. If the measurement were made by one of the standard methods,[4] in which the Polaroid is placed between the Raman tube and the lens which condenses the scattered light on the slit of the spectrograph and in which the Polaroid is rotated through an angle of 90° between the two exposures, the relative intensities would be those given in part *A* and part *B* of Table II, depending upon the position of the mercury arc. This, of course, assumes that correction has been made for the selective reflection of the polarized beams at the prisms of the spectrograph. Comparing these intensities with those obtained by the present method, part *C*, one finds that the same values of ρ would be obtained as in the standard method. *The present method, however, has the great advantage that, since the Polaroid remains fixed, there is no error caused by the polarization characteristics of the spectrograph.*[5]

Placing the Polaroid between the Raman tube and the spectrograph reduces the exposure time because it eliminates the strong absorption of the blue exciting light (Hg 4358A) before it reaches the Raman tube. The Raman lines (exclusive of the anti-Stokes lines) have longer wave-lengths and are not absorbed as greatly as the exciting light. While a Raman line of low displacement suffers a greater absorption in passing through the Polaroid than one of high displacement, this introduces no error into the results since only intensities of lines having the same displacement are compared in determining the values of ρ. The percentage of absorption of a given Raman line will be the same in the two exposures.

The use of a rather large slit width is made possible by the very complete absorption of the continuous mercury radiation by the filter solution employed.[1] The loss in resolution is more than compensated by the reduction in exposure time thus made possible.

Since the ratio of the densities of the lines on the polarization film is not the same as the ratio of the intensities of the light that produced them (unless the intensities happen to be identical), it was necessary to devise a method whereby the true intensity ratios could be obtained. In the method described above, the ratio of the intensity of the light which produced a given argon line in one of the weaker spectra to that of the light

[4] K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt* (Julius Springer, Berlin, 1931), p. 108.

[5] Cf. K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt, Ergänzungsband* (Julius Springer, Berlin, 1938), p. 84.

TABLE III. *Depolarization factors of the Raman lines of* CCl_4.

$\Delta\nu^*$ (cm^{-1})	I^*	CARRELLI-PRINGSHEIM-ROSEN†	CABANNES†	BHAGAVANTAM†	OUR RESULTS	TABLES ANNUELLES*
218	7	0.8	—	0.75	6/7	~6/7
314	8	0.9	—	0.8	6/7	~6/7
459	10	0.05	0.05	0.1	0.1	0.046
762	2	0.7	—	0.75	0.8	0.79
790	2			0.75	0.8	0.78
1535	0	—	—	0.33	—	0.3

* M. Magat, *Tables Annuelles* (Hermann & Cie, Paris, 1937), p. 26.
† Reference 4, p. 111.

TABLE IV. *Depolarization factors of the Raman lines of* C_6H_6.

$\Delta\nu^*$ (cm^{-1})	I^*	DAURE†	CARRELLI-PRINGSHEIM-ROSEN†	CABANNES†	BHAGAVANTAM†	OUR RESULTS	TABLES ANNUELLES*
606	5	—	1	~1	1	0.8	0.81
849	2	—	1	—	1	~6/7	0.77
992	10	<0.2	0.7	0.04	<0.05	0.1	0.07
1177	2	—	1	~1	—	0.8	0.70
1480	0	—	—	—	—	—	*D*
1585	3	—	1	~1	1	0.8	~6/7
1606	2						~6/7
2949	5	—	—	—	—	6/7	—
3046	4	>0.5	0.7	0.6	1	0.3	*D*
3063	8				0.35		0.4
3187	1	—	—	—	—	—	*P*

* M. Magat, *Tables Annuelles* (Hermann & Cie, Paris, 1937), p. 75–76.
† Reference 4, p. 111.

which produced the same line in the strongest spectrum is accurately known. Consequently, if the Raman pair on the polarization film matches these argon lines in density, it is evident that the ratios of the intensities of the Raman lines must be the same as that of the argon lines. Other conditions such as temperature, nature of the film, time of exposure, and wave-length region used in matching, must, of course, be held constant. One has in this method of comparing the intensities an absolute method which depends in no way upon any assumption as to the relation between the density of the line and the intensity of the incident light.

A most useful technique is that of adding a relatively small amount of CCl_4 to the liquid. One can then determine by rapid inspection whether there is any departure from the proper intensity in the two exposures by checking the depolarization factors of the strong CCl_4 lines against the accepted values. The percent of CCl_4 added should be small when the exposure time is great in order that its spectrum may not be so strong as to preclude accurate comparison of the intensities.

The present method is believed to be sufficiently easy in operation and accurate in its results to warrant the hope that future investigators may report depolarization factors for all the principal lines of the compounds which they study.

CHARACTERISTICS OF SPECTROGRAPH

The spectrograph was constructed from optical parts having the following characteristics: *Slit:* symmetrical slit, Gaertner *L162-b*; *collimating lens:* focal length 490 mm, aperture 52 mm; *two prisms:* glass, 60°, n_d 1.65, height 45 mm, base 75 mm; *camera lens:* focal length 400 mm, aperture 50 mm. The linear dispersion of the spectrograph is approximately 33A/mm at 4500A.

EXPERIMENTAL RESULTS

In order to test the method, the depolarization factors of the Raman lines of CCl_4 and C_6H_6, were determined from the spectra of a mixture containing approximately 15 percent CCl_4. Comparison of the values obtained with those of other workers is made in Tables III and IV. The exposure time was three hours for each position of the arc. Longer exposures would be necessary to obtain data for the weaker lines. The use of a comparatively wide slit prevented the resolution of the doublets 1585, 1606 and 3046, 3063. The use of a narrower slit and longer exposure times would be necessary to resolve these doublets.

The depolarization factors of a series of derivatives of phenylacetylene are being determined by this method. It has been found that three-fourths of an hour for each exposure is sufficient to give adequate density for the principal lines of these compounds.

ACKNOWLEDGMENTS

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Studies on Aging and Formation of Precipitates

XXIX. The Thermal Aging and Abnormal Physical Properties of Fresh Silver Bromide

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(1). Freshly precipitated silver bromide has a large surface development and is subject to thermal aging at room temperature in the air-dried state. During the aging the magnitude of the surface decreases and also the speed of incorporation of radioactive bromide, when bromine dissolved in ethyl bromide or in a gas phase is shaken with the solid. (2). A rapid exchange occurs between bromide in fresh air-dried silver bromide and radioactive bromine dissolved in ethyl bromide or bromine in the gas phase. (3). Fresh silver bromide has a relatively large electrical conductivity which is at least partly ionic.

FROM previous work carried out in this laboratory it was concluded that the main type of aging which occurs when a precipitate which consists of very small imperfect primary particles is kept in a liquid medium is the following. A rapid perfection of the primary particles takes place as a result of recrystallizations. The latter occur mainly in liquid films surrounding the particles. A precipitate consists of agglomerates containing a greater or smaller number of primary particles. When recrystallization of primary particles which constitute an agglomerate occurs, lattice material may be deposited in the interstices between the particles thus forming bridges and thereby cementing them together. This type of aging is irreversible; its speed depends in the first place upon the degree of perfection of the particles in the precipitate and upon the solubility of the precipitate in the liquid medium in which aging occurs, that is, in the liquid jacket around the particles. In the present study the aging of freshly precipitated silver bromide was investigated. The degree of aging and of perfection was followed by measuring the decrease of the specific surface as indicated by the amount of wool violet adsorbed on the surface saturated with the dye and by determining the speed of penetration of radioactive bromide ions into the inactive precipitate when the latter was shaken with a solution of the former. In one respect, the silver bromide behaved quite differently from other precipitates such as lead sulfate, lead chromate and barium sulfate investigated in this laboratory. It was found that when the solubility of the silver bromide in the aging medium had attained a certain minimum value a further decrease of the solubility did not affect the rate of aging. In Fig. 1 is given the change of the specific surface of fresh silver bromide aged at room temperature in 0.001 *M* silver nitrate in water (curve 1), in 0.001 *M* silver nitrate in ethanol (curve 2), and in benzene (curve 3). It is seen that a rapid decrease of the surface takes place during the early stages of aging and that the rate is not affected by the nature of the solvent in the above experiments. As a matter of fact, the rate of aging was found to be about equal to that of a precipitate kept in the air-dried state at 25°C (curve 4). In the latter case no recrystallization could take place by way of a liquid medium and the changes represented by the curves in Fig. 1 have been attributed to a thermal aging of the fresh silver bromide. This thermal aging was found to be very pronounced when the air-dried fresh silver bromide was heated for relatively short periods at 80° to 100°C. The other precipitates investigated in this

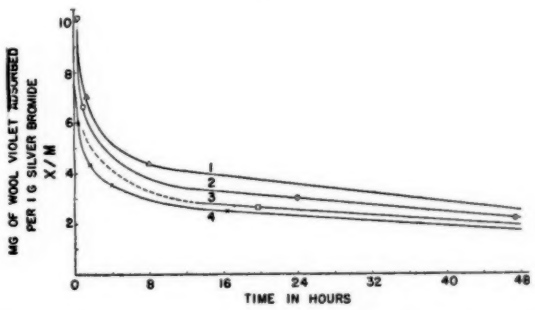

FIG. 1. Aging of silver bromide. △ 0.001 *N* $AgNO_3$, water; ⊙ 0.001 *N* $AgNO_3$, ethanol; ⊡ benzene; × air-dried.

laboratory could be kept unchanged indefinitely at 100°C. From conductance work it may be inferred that the thermal mobility of the ions in the lattice of well-aged silver bromide is extremely small. From our work we infer that the thermal mobility of silver bromide on active surface is very marked even at room temperature. The ions or molecules on the active surface can move over to more normal surface. This "recrystallization" gives rise to a perfection and to a decrease of the total surface of the precipitate. To substantiate the above view, experiments were carried out in which fresh silver bromide was shaken with a solution of radioactive bromine in ethyl bromide. The solubility of silver bromide in this organic solvent is negligibly small, any exchange between active bromine and inactive bromide beyond the surface layer, therefore, is to be attributed to a thermal aging of the solid:

$$\underset{\text{Solution}}{\tfrac{1}{2}Br_2} + \underset{\text{Surface}}{Br^-} \rightleftharpoons \underset{\text{Solution}}{\tfrac{1}{2}Br_2} + \underset{\text{Surface}}{Br^-} \quad . \quad (1)$$

When fresh surface is exposed continuously as a result of the thermal aging much more radioactive bromide will be incorporated in the precipitate than would correspond to the original surface of the particles. As shown below this was actually found.

In order to eliminate the possibility of any recrystallization by way of the solution fresh air-dried silver bromide was shaken with radioactive bromine in the gaseous phase. Again, incorporation of radioactive bromide in the solid occurred as a result of thermal aging. Incidentally, it may be mentioned that the latter experiments show that a free transfer of electrons occurs between bromine (in gas or liquid phase) and bromide ions on the surface of silver bromide.

Experimental

The preparation of silver bromide and of active bromine and the determination of the radioactivity is described in detail in the thesis of Junior author.[1] Radioactive bromine was prepared by suspending soft glass bulbs, containing approximately 100 mg of beryllium and from 100–140 millicuries of radon[2] in one liter of dry C.P. ethyl bromide which contained 7.5 to 8 milli-equivalents of bromine. After an exposure of 18 hours enough of the 4.5-hour isotope was present to carry out the experiments. In the experiments with radioactive bromine gas we proceeded in a similar way. After the radiation, the bromine was reduced and extracted with sodium bisulfite solution. After addition of 0.7 g of inactive potassium bromide and 10 ml of 6 *N* sulfuric acid the excess of sulfur dioxide was removed by boiling and the volume was reduced to 20 ml. One gram of potassium bromate was added to the cooled solution and the bromine formed was drawn slowly through a drying tube containing anhydrous calcium chloride and collected in a 2½-liter dry, glass stoppered bottle. A one-liter bottle was filled in the same way with bromine vapor to be used as a standard in the measurements.

The radioactivity of a residue in a 17-ml copper dish was measured by placing the latter in the holder under the aluminum window of an ionization chamber, across which a potential of 180 volts was maintained. The resulting current after sufficient amplification was measured with a very sensitive galvanometer. The amplifying circuit, constructed with the aid of Dr. C. S. Copeland was essentially the one recommended by DuBridge and Brown.[3] In none of the experiments were readings made before three hours had elapsed from the time of removal of the beryllium radon bulb.

Exchange Between Radioactive Bromine in Ethyl Bromide and Fresh Silver Bromide

Silver bromide was obtained by adding 100 ml of 0.426 *M* potassium bromide to 100.5 ml of 0.426 *M* silver nitrate. The precipitate was filtered on a sintered glass funnel, washed with water, ethanol, ether and ethyl bromide, and then air-dried until the odor of ethyl bromide was no longer perceptible. Two gram samples were placed into dry 250-ml glass stoppered

[1] Doctor's thesis submitted by Albert S. O'Brien to the Graduate School of the University of Minnesota (June, 1938).

[2] We wish to thank Dr. D. Hull of the Division of Physical Chemistry of this University for his kindness in supplying us with the radon bulbs.

[3] L. DuBridge and H. Brown, Rev. Sci. Inst. **4**, 532 (1933).

bottles, to which 200 ml of ethyl bromide containing radioactive bromine was added. The silver bromide samples were exactly 20 minutes old at the time of addition of ethyl bromide. All of the experiments were carried out in duplicate. One set of bottles was shaken for 70 minutes, and another for 3½ hours. At the end of the shaking period the silver bromide was filtered and washed five times with carbon tetrachloride to remove all of the adsorbed bromine. The silver bromide residue was spread in a thin layer on a copper dish and the activity measured.

The bromine in the filtrate was reduced and extracted in a separatory funnel with 10 ml of an aqueous sodium bisulfite solution. The latter plus 5 ml of water used to rinse the funnel and a slight excess of sodium hydroxide was evaporated to dryness in a copper dish. Later it appeared that not all of the radioactive bromine was extracted by this procedure and that about 25 percent was lost. Blank experiments showed that this loss was constant and that it did not affect the results. A check was obtained by the measurement of the activity of the silver bromide.

In order to see whether the speed of removal of the radioactive bromine from the solution in ethyl bromide decreased with increasing age of the precipitate, the following additional experiments were made. Samples of the fresh air-dried product were aged for 1 hour and for 19 hours, respectively, in ethyl bromide before they were shaken with the radioactive bromine solution. Also, a drastically aged product was prepared by digesting a precipitate in 0.5 *M* potassium bromide for 5 days at 95°C, it was then filtered, washed and made air-dry. Only 0.04 to 0.05 percent of all the bromide in the solid was present in the surface of the latter product, while about 2 percent of all the bromide was in the surface of the fresh product. The results are given in Table I. The reported values of *R* refer to the ratio of radioactive bromine removed to that left in the solution per 1 g of silver bromide. If the exchange were limited to the surface we would find (see Eq. (1))

$$R=\frac{\text{Br}^{-*}\text{ removed}}{\frac{1}{2}\text{Br}_2^{*}\text{ left}}=\frac{\text{Br}^{-}\text{ surface}}{\frac{1}{2}\text{Br}_2\text{ solution}}.$$

In this case *R* would be less than 0.05 for the freshest product. If, on the other hand, exchange had taken place with all of the bromide in the precipitate we would find

$$R=\frac{\text{Br}^{-*}\text{ removed}}{\frac{1}{2}\text{Br}_2^{*}\text{ left}}=\frac{\text{Br}^{-}\text{ precipitate}}{\frac{1}{2}\text{Br}_2\text{ solution}}=2.84.$$

The large values of *R* found with the fresh (20 minutes old) product indicate a heterogeneous distribution of the active bromide through the solid. From the results it is evident that the exchange is not limited to the surface and that it extends throughout the precipitate. The speed of penetration decreases with increasing age of the precipitate.

TABLE I. *Speed of exchange of radioactive bromine in ethyl bromide with silver bromide of various age.*

AGE OF AgBr	TIME OF SHAKING WITH Br*	ACTIVITY REMOVED IN % PER 1 g AgBr	*R*
20 minutes	70 minutes	75.5	3.08
20 minutes	3½ hours	82.1	4.6
1 hour	40 minutes	60	1.5
1 hour	90 minutes	62.5	1.7
19 hours	70 minutes	50	1.0
19 hours	3½ hours	66.5	2.00
Drastically aged[a]	70 minutes	1.4	0.014
Drastically aged[a]	4 hours	6.2	0.07

[a] No measurable activity was found in the solid after shaking.

EXCHANGE BETWEEN RADIOACTIVE BROMINE GAS AND SILVER BROMIDE

Fresh silver bromide was prepared as above, after the washing with ether, air was drawn through until the odor of ether was no longer perceptible. A one-gram sample was placed in a 2½-liter bottle containing the radioactive bromine gas and the whole shaken at frequent intervals for a total period of 100 minutes. At the end of the shaking, 40 ml of carbon tetrachloride was added to the bottle and the contents were vigorously shaken. The silver bromide was filtered at once and washed five times with large portions of carbon tetrachloride to remove adsorbed bromine. The silver bromide was air-dried and spread in a thin layer on the bottom of a copper dish. The bromine in the carbon tetrachloride was reduced and extracted with sodium bisulfite solution and the extract evaporated to dryness in alkaline medium in a copper dish. The standard bottle with 1 liter of bromine was

treated in a similar way. The activity of each dish was determined. Moreover the total amounts of bromide in the experimental and standard dishes were determined by a volumetric procedure.[4]

It was calculated that about 0.55 percent of the active bromine would have been removed if the exchange had been limited to the surface, whereas 59.5 percent would have been removed if exchange with all of the bromide ions in the silver bromide (homogeneous distribution) had taken place. Actually 38.2 percent of the active bromine was found removed, showing that many layers of silver bromide beyond the surface had participated in the exchange.

Reverse experiments were carried out by shaking fresh radioactive silver bromide with inactive bromine gas. The solid was prepared by adding a slight excess of silver nitrate to a radioactive bromide solution. The precipitate was filtered, washed with water, alcohol and ether and air-dried. Two gram samples of the solid were transferred to a dry 2.5-liter bottle containing approximately 2.5 grams of inactive bromine. The bottle was shaken at frequent intervals for 30 minutes before extracting the bromine with carbon tetrachloride. The activities of the solid and of the extracted bromine were determined in a similar way as described above. The results indicated that about 30 percent of all the bromide in the solid had participated in the exchange with the inactive bromine.

Finally, experiments were carried out in which fresh air-dried silver bromide was shaken with a solution of radioactive iodine in ethyl iodide. The results indicated that a marked exchange occurred between bromide in the solid and iodine in the liquid:

$$\underset{\text{solid}}{Br^-} + \underset{\text{liquid}}{\tfrac{1}{2}I_2} \rightarrow \underset{\text{solid}}{I^-} \quad \underset{\text{liquid}}{\tfrac{1}{2}Br_2}.$$

Electrical Conductivity of Fresh Silver Bromide

The great thermal mobility of fresh silver bromide at 25°C suggested a relatively great electrical conductivity of this substance. This was shown to be true; however, the exact interpretation of the results was complicated by the fact that the pellets of fresh silver bromide continued to decrease in size markedly and continuously with increasing age. Cylindrical pellets, about 1.25 cm in diameter and 0.6 cm long were prepared in the dark from 2 g of fresh air-dried silver bromide. A pellet was clamped between two silver-plated copper electrodes across which an electromotive force of 6 volts was applied. The current as indicated by a microammeter varied from 40 to 110 microamperes with different pellets. Upon aging of the pellets the apparent resistance changed in an irregular way; the interpretation of the results being complicated by the changing compressibility of the pellet. At present, Mr. I. Shapiro in this laboratory is making a more detailed study of the electrical conductivity of fresh silver bromide. His experiments have shown already that at least part of the conductance is ionic. Further work is in progress to determine the transference numbers of silver and bromide ions in fresh silver bromide and to find out whether the conductance is partly electronic.

[4] I. M. Kolthoff and H. C. Yutzy, Ind. Eng. Chem. Anal. Ed. **9**, 75 (1937).

An Equilibrium Theory of Ionic Conductance

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(Received March 29, 1939)

A theory for ionic conductance which assumes that the equilibrium between the central ion and its ionic atmosphere is not appreciably distorted by the application of the external field is proposed. On the basis of this approach, values of the radii for the individual ion are obtained by the extrapolation of conductance and transference data to infinite dilution. These values of the radii when inserted into the equations resulting from the theory yield expressions for conductance and transference that very closely follow the experimental ones up to $0.02M$. Even at concentrations as high as molar, the discrepancy between the equilibrium theory and experiment is not large. The values of the ionic radii obtained from the theory are also correlated with the corresponding values of equivalent conductances at infinite dilution. The larger the ion, the more closely does it appear to obey the laws of classical hydrodynamics. For smaller ions, deviations from classical hydrodynamics increase rapidly as the radius decreases. On this basis, the high conductance of hydronium ion appears to follow naturally from the small radius obtained, namely, 0.95A. Furthermore, the deviation from the classical theory appears to be given by an expression involving the size of the hole that the ion must make in order to jump from equilibrium position to equilibrium position in the solvent, an idea suggested by the modern theory of liquids as developed by Eyring and his collaborator.

THE widely accepted theories of Onsager,[1] Debye and Hückel[2] and others for the conductivity of electrolytes in polar solvents were developed for point charges. It is inherent in these theories that a considerable portion of the observed decrease of the equivalent conductance with increasing salt concentration is to be attributed to a distortion of the ion atmosphere of the central ion by the applied external field. Thus arise considerations of the "relaxation time" and of "relaxation effects" in the treatment of conductance problems.

It was thought to be of interest to investigate the effects of the finite size of the ions on the conductance of electrolytes and to include them, if possible, in the theory. The development was started by assuming that the application of the external field does not distort the ionic atmosphere surrounding the central ion. The equations derived on this basis have novel properties. They predict the limiting law of Kohlrausch. Furthermore, in the simplest case (positive and negative ion are of the same size), the ionic radii are related in a simple way to the limiting slope at infinite dilution of a plot of the equivalent conductance against the square root of the ionic strength. Lastly, the values of the ionic radii obtained in this way are reasonable and when inserted into the equations predict, within the experimental error, the course of the equivalent conductance up to about $0.02M$. At concentrations as high as molar, the deviation between the equilibrium theory and experiment is not large. For ions unlike in size, the theory appears to apply equally well. For instance, predicted values of the transference numbers correspond very closely with the experimental ones up to $0.1M$ or higher. It appears, therefore, that with not too rapidly oscillating fields of strength below which the Wien effect appears, the experimental values for the conductance as a function of the ionic strength may be derived theoretically without considering relaxation effects.

The values of the individual ionic radii obtained by this method from conductance data were found to be related in a simple way to the corresponding values of the equivalent conductances at infinite dilution. It will be demonstrated that the larger the ion the more closely does the experimental value of the equivalent conductance at infinite dilution agree with the value demanded by classical hydrodynamics. For smaller ions the deviation increases rapidly with decreasing radii, until at values of the radius about that of hydronium ion (0.95A), not even the order of magnitude is predicted by the classical theory. These deviations appear to follow naturally from the modern notions of liquids as developed by Eyring,[3] and his collaborators. On the basis of

[1] L. Onsager, Physik. Zeits. **27**, 388 (1926); **28**, 277 (1927).
[2] P. Debye and E. Hückel, Physik. Zeits. **24**, 305 (1923).
[3] H. Eyring, J. Chem. Phys. **4**, 283 (1936).

these theories, the high conductances of hydronium and hydroxyl ion may be qualitatively explained. The activated jumps of the hydronium ion from equilibrium position to equilibrium position in the liquid replace the more specific jumps of the proton from water molecule to water molecule given in the theory of Bernal and Fowler,[4]

It should be emphasized that the theory about to be presented is not an "electrophoretic theory," in the sense that it does not depend upon classical hydrodynamics. Rather it depends only upon the notions which are inherent in all theories, that the mobility of the ion will be directly proportional to the potential at its surface and that this potential may be obtained by the approximations of Debye and Hückel.[2] In addition, two other notions are involved; the first is that the central ion with its ion atmosphere does not appreciably distort[5] the applied external field and the second is that the applied external field does not sensibly distort the ionic atmosphere of the central ion. The second notion may be expressed as follows: the equilibrium between the central ion and its ionic atmosphere is not disturbed to an appreciable extent by the application of an external field.

The Equilibrium Theory

The equilibrium theory for the potential of large ions in solutions containing an excess of ordinary electrolytes was developed in one of the early papers of Debye and Hückel[2] Abramson[6] and later Moyer[7] applied it with considerable success to proteins. Using the equations of Henry,[5] which are based upon classical hydrodynamics and combining them with potential equations based upon the equilibrium theory for large ions, Abramson[6] found that the predicted and observed mobilities agreed within 60 percent. In the theory, as it was heretofore applied, only the dimensions of the large central ion were taken into consideration. The ions of the ordinary electrolytes present in the solution, which make up the ionic atmosphere of the large central ions, were assumed to be point charges.

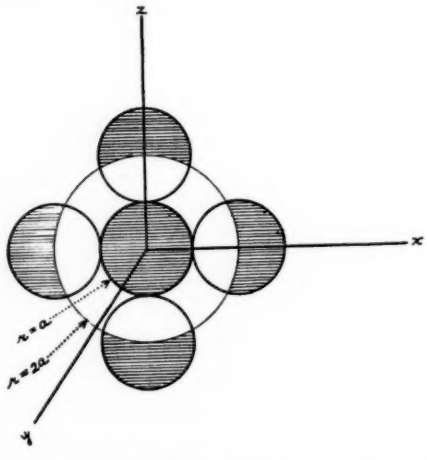

Fig. 1. Schematic representation of the potential problem for electrolytes made up of spherical ions of identical size.

It was found by the author[8] of this paper that the finite size of the other ions present in the solution (sodium and acetate for instance) should theoretically exert considerable influence upon the surface potential of the large central ion. Equations which included the size of the other ions were successfully applied to protein ions.

Ions of the same size

The theory will now be developed for solutions of ordinary electrolytes by considering the simple case in which the positive and negative ions of the salt have the same dimensions (see Fig. 1). The ions will be considered to be spherically symmetric and of definite size. By the concept of definite size is not meant a constant, unchanging radius. Rather, it is implied that a distinction must be made between two types of interactions of the central ion with the solvent molecules. One results in a firm binding of the solvent molecule to the central ion and for the lack of a better term will be called the *chemical interaction*. The other, while fundamentally brought about by the same type of forces, results only in bonds too weak to allow the ion and the solvent mole-

[4] J. D. Bernal and R. H. Fowler, J. Chem. Phys. **1**, 515–48 (1933).

[5] See D. C. Henry, Proc. Roy. Soc. (London) **A133**, 106 (1931).

[6] H. A. Abramson, *Electrokinetic Phenomena* (Chemical Catalog Co., Inc., New York, 1934).

[7] L. S. Moyer, Cold Spring Harbor Sym. Quant. Biol. **6**, 228 (1938).

[8] Not as yet published in full. For preliminary report see H. A. Abramson, M. H. Gorin and L. S. Moyer, Chem. Rev (in press) (1939).

cule to remain together as a *diffusing unit.* It might be called the *viscous interaction.* This distinction is of importance both for the potential and for the hydrodynamic problems.

Hydrodynamically, either for the classical or the Eyring[3] point of view, the radius to be considered is the radius at the point of shear between the ion and the solvent. Therefore it is seen that the solvent molecules, which chemically interact with the central ion and are therefore firmly bound, must be included in the radius, for obviously they are inside the *surface of shear.* On the other hand, solvent molecules outside the surface of shear viscously interact with the ion.

Similarly, for the potential problem, the radius of the ions must be taken as half the distance (considering ions of identical size) between the positive and negative ions at the point of closest approach. In the development that follows, it is assumed that the ions constituting the ionic atmosphere do not penetrate inside the shell of firmly bound solvent molecules that surround the central ion, but rather that they come up, at the point of closest approach, only to the surface of shear. On this basis the radii for the potential problem and the hydrodynamic problem are identical.

Potential problem for ions of identical sizes

The coordinate system will be polar with $r=0$ at the center of the central ion. The potential, ψ, is assumed to be a function of r alone. From $r=0$ to $r=2a$, where a is the ionic radius (see Fig. 1), the only charge present is that on the central ion and from $r=a$ to $r=2a$ no charges are present. Therefore in the region bounded by the surfaces $r=a$ and $r=2a$ the potential is a solution of Laplace's equation:

$$\nabla^2\psi_{a\to 2a}=0$$

or in polar coordinated with spherical symmetry

$$\frac{d^2\psi_{a\to 2a}}{dr^2}+\frac{1}{r}\frac{d\psi_{a\to 2a}}{dr}=0. \tag{1}$$

The solution of (1) is

$$\psi_{a\to 2a}=A/r+B, \tag{2}$$

where A and B remain to be fixed. From $r=2a$ to $r=\infty$ charges are present and therefore ψ is a solution of Poisson's equation

$$\nabla^2\psi_{2a\to\infty}=-4\pi\rho/D, \tag{3}$$

where ρ is the charge density and D the dielectric constant. Proceeding by the method of Debye and Hückel ρ is replaced by

$$n\mathbf{e}(\exp(-\mathbf{e}\psi/kT)-\exp(+\mathbf{e}\psi/kT)),$$

where n is the number of ions per cc and $\mathbf{e}$ the electronic charge, and with the usual assumption that $\sinh \mathbf{e}\psi/\mathbf{k}T$ may be replaced by $\mathbf{e}\psi/\mathbf{k}T$ the well-known equation[9] is obtained

$$\psi_{2a\to\infty}=\frac{e}{Dr}\frac{e^{-\kappa(r-2a)}}{1+2\kappa a},$$

where e is the charge on the central ion and κ is given by

$$\kappa=(4\pi\mathbf{N}\mathbf{e}^2/1000D\mathbf{k}T)^{\frac{1}{2}}(2\mu)^{\frac{1}{2}}.$$

$\mathbf{N}$ is Avogadro's number and μ is the familiar ionic strength function. To obtain $\psi_{a\to 2a}$ (4) and (2) can be smoothly joined at $r=2a$. Therefore, at $r=2a$,

$$\psi_{a\to 2a}=\psi_{2a\to\infty}$$

and

$$d\psi_{a\to 2a}/dr=d\psi_{2a\to\infty}/dr$$

or

$$A/2a+B=e/2Da(1+2\kappa a)$$

and

$$-A/4a^2=-e/4Da^2 \tag{5}$$

From (5) A and B may be obtained and the following results:

$$\psi_{a\to 2a}=e/Dr-e\kappa a/Da(1+2\kappa a). \tag{6}$$

As was stressed before, the potential of importance in conductance problems is the potential at the surface of shear, or, therefore, the potential at $r=a$. This potential is commonly called the ζ-potential and will be so designated. From (6) it follows that

$$\psi_{r=a}=\zeta=\frac{e}{Da}\left(\frac{1+\kappa a}{1+2\kappa a}\right). \tag{7}$$

The novel feature of (7) is the appearance in the numerator of the function $(1+\kappa a)$.

For ions of different sizes the treatment is practically identical. No details of the derivation

[9] See, for instance, H. A. Abramson, reference 6, p. 103.

will be given. One additional assumption is involved. It is that interactions between ions of like sign in the neighborhood of their surface of shear may be neglected. For salts made up of positive ions of radius a and negative ions of radius b it follows, then, that:

$$\left.\begin{aligned}\zeta_+&=\frac{e}{Da}\left(\frac{1+\kappa b}{1+\kappa(a+b)}\right)\\ \zeta_-&=\frac{e}{Db}\left(\frac{1+\kappa a}{1+\kappa(a+b)}\right)\end{aligned}\right\}. \tag{8}$$

Application of the equilibrium theory to conductance of electrolytes

The mobility of an ion in an electric field is proportional to the potential at its surface of shear (ζ-potential), assuming that there is no distortion of the external field by the central ion or its ionic atmosphere. Henry[5] has exhaustively investigated the problem of the distortion of the external field. On the basis of his results, it is easily shown that for the ions in solutions of ordinary electrolytes (radius less than 5A) the distortion of the external field by the central ion with its ionic atmosphere is negligible even at molar concentrations. It then follows that the equivalent conductances of the individual ions, Λ_+ and Λ_-, respectively, will be given by

$$\Lambda_+=C_{r+}\zeta_+, \quad \Lambda_-=C_{r-}\zeta_-,$$

where C_r is a function of the radius, r, alone. The equivalent conductance, Λ, of the salt is

$$\Lambda=\Lambda_++\Lambda_-=C_{r+}\zeta_++C_{r-}\zeta_-. \tag{9}$$

For salts in which both ions are of the same size and of radius a, assuming that the central ions are at equilibrium with their ionic atmosphere, the equivalent conductance becomes from (9) and (7)

$$\Lambda=\frac{2C_ae}{Da}\left(\frac{1+\kappa a}{1+2\kappa a}\right). \tag{10}$$

At infinite dilution

$$\Lambda=\Lambda^0=2C_a/aD.$$

Therefore (10) becomes

$$\Lambda=\Lambda^0(1+\kappa a)/(1+2\kappa a). \tag{11}$$

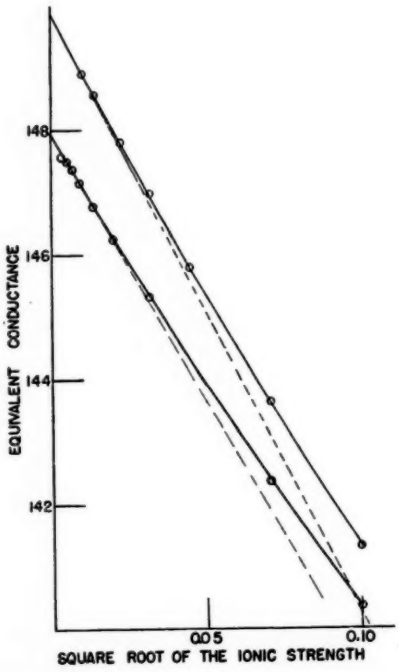

FIG. 2. Comparison of equilibrium theory with experiment. Upper curve Λ for KCl at 25° (data from Shedlovsky). Lower curve ($\Lambda+18$) for KCl at 18°. The smooth curves were calculated by the equilibrium theory. The dashed curves represent the limiting slopes.

It is obvious that for the positive and negative ions to have the same radius Λ_+ must equal Λ_- always assuming, of course, spherical symmetry. In practice it was found the (11) gives good agreement with salts like KCl or $LiIO_3$ for which Λ_+ and Λ_- are nearly equal.

Since κ is proportional to the square root of the ionic strength, (11) may be written

$$\Lambda=\Lambda^0(1+c\mu^{\frac{1}{2}})/(1+2c\mu^{\frac{1}{2}}), \tag{12}$$

where $c=a(8\pi\mathbf{N}\mathbf{e}^2/1000D\mathbf{k}T)^{\frac{1}{2}}$.

For water at 25° $c=3.279\times10^7a$ and at 18° $c=3.268\times10^7a$. It is easily shown by differentiating (12) that as $\mu\to0$

$$d\Lambda/d\mu^{\frac{1}{2}}=-c\Lambda^0. \tag{13}$$

Thus (12) obeys the limiting law of Kohlrausch.

In Fig. 2 the exceedingly accurate results of Shedlovsky[10] for the equivalent conductance of potassium chloride solutions of various concentrations are plotted against the square root of the

[10] T. Shedlovsky, J. Am. Chem. Soc. **54**, 1411 (1932).

ionic strength. The limiting slope was judged to be -96.1 and Λ^0 was taken as 149.86, slightly higher than the extrapolated value of Shedlovsky.[10] By (13) then, $c=0.641$. Inserting this value in (12) the function

$$\Lambda=149.86(1+0.641\mu^{\frac{1}{2}})/(1+1.282\mu^{\frac{1}{2}}) \quad (14)$$

was plotted. It is represented by the solid curve in Fig. 2 (upper). The dotted line represents the limiting slope. It may be seen that the experimental points fall on the curve representing (14) within the experimental error (maximum deviation in $\Lambda=0.02$) in the region considered, $\mu=0$ to 0.01. At higher concentration the agreement is still good, but the discrepancy at $0.1M$ is considerably larger than the experimental error, as may be seen below.

μ	$\Lambda_{(14)}$	Λ_{exp}
0.02	138.35	138.34
0.10	128.25	128.90

In Fig. 2 are also plotted the excellent older data[11] of Kohlrausch and Maltby for KCl at 18°. The solid curve (lower) corresponds to the equation

$$\Lambda=129.92(1+0.657\mu^{\frac{1}{2}})/(1+1.314\mu^{\frac{1}{2}}) \quad (15)$$

and the dotted line to the limiting slope predicted by (15). The experimental points (circles) fall on the solid curve within the experimental error. At higher concentrations (15) gives the values in Table I. The last column of the table is the value of Λ predicted by the dotted line (limiting slope), which corresponds to the relaxation theory. The values of a (the average ionic radius) corresponding to c are 1.95 and 2.01A at 25° and 18°, respectively.

Another salt for which Λ_+ and Λ_- are nearly equal is lithium iodate. In a plot of Λ against $\mu^{\frac{1}{2}}$ of the data[12] for lithium iodate the values, 67.35 and 1.085, were found for Λ^0 and c, respectively. Therefore the function predicted by the equilibrium theory is

$$\Lambda=67.35(1+1.085\mu^{\frac{1}{2}})/(1+2.170\mu^{\frac{1}{2}}). \quad (16)$$

In Table II, the values of Λ predicted by (16) are compared with the experimental ones.

It may be seen from Table II that the conductances of $LiIO_3$ demanded by the equilibrium theory, $\Lambda_{(16)}$, agree with the actual ones, Λ_{exp}, within the experimental error up to $0.01M$, and furthermore, that the discrepancy between theory and experiment is small even at $0.1M$.

The value of c, 1.085, in (16) corresponds to 3.32A for the average radius of the ions of lithium iodate, Li^+ and IO_3^-.

TABLE I.

μ	$\Lambda_{(13)}$	Λ_{exp}	$\Lambda^0(1-c\mu^{\frac{1}{2}})$
0.02	119.73	119.72	117.85
0.10	110.86	112.0	102.93
1.00	93.03	98.3	44.56

TABLE II. *Comparison of equilibrium theory with experimental data for* $LiIO_3$ *at 18°.*

M	$\Lambda_{(16)}$	Λ_{exp}
0.0001	66.63	66.57
.0002	66.35	66.34
.0005	65.79	65.78
.0010	65.19	65.18
.0020	64.37	64.34
.0050	62.87	62.80
.0100	61.35	61.15
.0200	59.44	58.97
.1000	53.65	51.43

CONDUCTANCE AND TRANSFERENCE OF SALTS MADE UP OF IONS OF DIFFERENT RADII

Individual ionic radii

For a solution of a salt whose positive and negative ions are of radius a and b, respectively, (8) gives:

$$\left.\begin{aligned}\zeta_+&=e(1+\kappa b)/Da(1+\kappa(a+b)),\\ \zeta_-&=e(1+\kappa a)/Db(1+\kappa(a+b)).\end{aligned}\right\}$$

Or, by the method used above, it is easily obtained that the conductance, Λ, of the salts should be

$$\Lambda=\Lambda^0_+\left(\frac{1+\kappa b}{1+\kappa(a+b)}\right)+\Lambda^0_-\left(\frac{1+\kappa a}{1+\kappa(a+b)}\right), \quad (17)$$

where Λ^0_+ and Λ^0_- are the individual equivalent conductances of the positive and negative ions

[11] See article by J. R. Partington in Taylor's *Physical Chemistry*, second edition (D. Van Nostrand, New York, 1931), p. 659.

[12] *Int. Crit. Tables*, 6, 241 and 247.

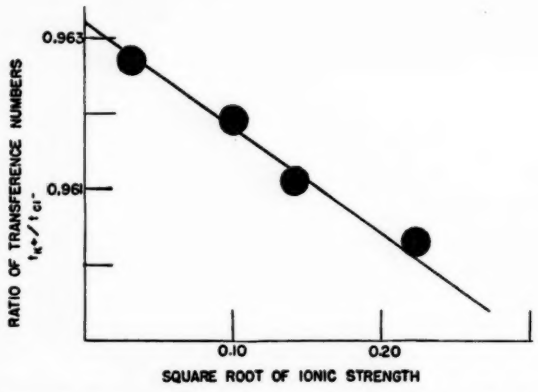

FIG. 3. Extrapolation of transference number ratios for KCl to infinite dilution. Data from Longsworth, reference 13. This method is very similar to that of T. Shedlovsky, J. Chem. Phys. **6**, 845 (1938). The extrapolated value of t^0_+ for KCl given by the two methods is identical, 0.4906.

at infinite dilution. At 25° (17) gives

$$\Lambda=\Lambda^0_+\left(\frac{1+3.279\times10^7 b\mu^{\frac{1}{2}}}{1+3.279\times10^7(a+b)\mu^{\frac{1}{2}}}\right)+\Lambda^0_-\left(\frac{1+3.279\times10^7 b\mu^{\frac{1}{2}}}{1+3.279\times10^7(a+b)\mu^{\frac{1}{2}}}\right). \quad (18)$$

Differentiating (18), the following is obtained as $\mu\rightarrow0$:

$$d\Lambda/d\mu^{\frac{1}{2}}=-3.279\times10^7(\Lambda^0_+a+\Lambda^0_-b). \quad (19)$$

Also, of course,

$$\Lambda^0=\Lambda^0_++\Lambda^0_-. \quad (20)$$

Thus, in a plot of Λ against $\mu^{\frac{1}{2}}$, the extrapolated value, Λ^0, and the estimated initial slope furnish two of the four equations necessary to obtain the four parameters in (17), a, b, Λ^0_+ and Λ^0_-. The two other equations needed can be similarly obtained by extrapolation of transference data. For this purpose taking the positive ion as the example, the function most easily extrapolated is not the transference number, $\Lambda_+/\Lambda_++\Lambda_-$, but the ratio of the transference numbers for the positive and negative ions, Λ_+/Λ_-. It is easily seen from (17) that the equilibrium theory yields for this ratio the following:

$$\Lambda_+/\Lambda_-=\Lambda^0_+/\Lambda^0_-(1+\kappa b)/(1+\kappa a)$$

or at 25°,

$$T_+=T^0_+\left(\frac{1+3.279\times10^7 b\mu^{\frac{1}{2}}}{1+3.279\times10^7 a\mu^{\frac{1}{2}}}\right), \quad (21)$$

where the definitions of T_+ and T^0_+ are obvious. Then, from (21) as $\mu\rightarrow0$:

$$dT/d\mu^{\frac{1}{2}}=-3.279\times10^7T^0_+(b-a). \quad (22)$$

In general, accurate transference data is not available in very dilute solutions. However, the excellent data of Longsworth[13] extend down to $0.001M$ for potassium chloride. Since only the values for the ions of one salt are needed to obtain the values of Λ^0 for all the individual ions, there are no difficulties in interpreting the data in terms of the equilibrium theory for the other salts.

If $(b-a)$ is small, (21) may be replaced by

$$T_+=-T^0_+3.279\times10^7(b-a)\mu^{\frac{1}{2}}, \quad (23)$$

which demands that T_+ should be proportional to $\mu^{\frac{1}{2}}$. In Fig. 3, the very accurate data of Longsworth[13] are plotted. The points scatter about the straight line chosen but the deviations from the line are within the experimental error. The value obtained for T^0_+ is 0.9632 ∓ 0.0002 and for the slope -0.014 ∓ 0.001. Combining (23), (19) and (20) the following were obtained for potassium chloride at 25°:

$$\left.\begin{aligned}\Lambda^0_+&=\Lambda^0_{K^+}=73.53\pm0.02\\ \Lambda^0_-&=\Lambda^0_{Cl^-}=76.33\pm0.02\\ a&=r_{K^+}=1.978\text{A}\pm0.004\\ b&=r_{Cl^-}=1.933\text{A}\pm0.004\end{aligned}\right\}. \quad (24)$$

By inserting (24) in (17) Table III was calculated.

It is demonstrated in Table III that the equilibrium theory represents the experimental data well, both for conductance and transference.

Since $\Lambda^0_{Cl^-}$ at infinite dilution has been fixed, the function T^0_+ can now be obtained for all other chlorides, without extrapolating transference data. An extrapolation of the conductance of the salt to infinite dilution and the estimated limiting slope combined with the known value of Λ^0_- furnish three of the four equations needed to determine the four parameters of (17). The fourth equation can be obtained

[13] L. G. Longsworth, J. Am. Chem. Soc. **54**, 2741 (1932); see also D. Mac Innes, T. Shedlovsky and L. G. Longsworth, J. Am. Chem. Soc. **54**, 2758 (1932).

by inserting into (21) the value of T_+, calculated from transference data at the lowest concentration at which it is available.

To illustrate this method the data of Shedlovsky[10] and Longsworth[13] for sodium chloride will be used. Shedlovsky's data were extrapolated in a plot similar to Fig. 2. It was decided that:

$$\left.\begin{aligned} \Lambda_0 &= 126.45 \\ d\Lambda/d\mu^{\frac{1}{2}} &= -90.57 \quad \text{at} \quad \mu = 0 \end{aligned}\right\}.$$

To these data must be added those of Longsworth[13] for the transference number of sodium ion in sodium chloride at $0.01M$ (lowest concentration at which his measurements are available) $t_+ = 0.3918$.

Then of course it follows immediately that,

$$\Lambda^0_{Na^+} = 126.45 - 76.33 = 50.12;$$

and that $T^0_+ = 50.12/76.33 = 0.6566$,

while $T^{0.01}_+ = 0.3918/1 - 0.3918 = 0.6442$.

The two equations needed to fix a and b become

$$\left.\begin{aligned} 90.57 &= 3.279\times10^7(50.12a + 76.33b) \\ 0.6442 &= 0.6556\left(\frac{1+3.279\times10^7(0.1b)}{1+3.279\times10^7(0.1a)}\right) \end{aligned}\right\}; \quad (25)$$

and from (25)

$$a = r_{Na^+} = 2.562\text{A} \quad \text{and} \quad b = r_{Cl^-} = 1.937\text{A}.$$

The close agreement between the radii for chloride ion obtained from the two salts, KCl and NaCl, 1.933 and 1.937A, respectively is suggestive. In Table V, (17) is compared with the data of Shedlovsky[10] and Longsworth[13] for sodium chloride.

Two other chlorides, for which the accurate measurements of these authors[10, 13] are available, are lithium chloride and hydrochloric acid. For these electrolytes, a, b, Λ_+ and Λ_- were obtained as above. The results together with those for NaCl and KCl are shown in Table IV.

A discussion of the significance of the values of the individual ionic radii given in Table IV will be given in the next section.

In Table V, the results obtained for conductance and transference by inserting in (17) the values of a, b, Λ^0_+ and Λ^0_- given in Table IV are compared with the actual results of Shedlovsky[10] and Longsworth[13] for sodium, lithium and hydrogen chloride at 25°.

Ionic radii by other methods

The excellent agreement between the equilibrium theory and experiment (Fig. 2, Tables II, III, IV and V) can be further extended by independent methods of estimating the individual ionic radii. While the values obtained are reasonable, it remains to be shown that they are physically associated with those demanded by the model from which they were calculated.

The ions at the two extremes in Table IV, H_3O^+ and Li^+ will, be considered. If hydronium ion were unhydrated its radius would be about equal to the O−H distance in water, 0.95A. The value given in Table IV, 0.945A is in excellent agreement with the above supposition. That hydronium ion is probably unhydrated is suggested by estimates of the amount of water it transports. These are obtained by comparing the Hittorf transference number with the "true transference" number.[14] On the same basis (transference numbers versus Hittorf numbers), lithium ion transports at least six water molecules. The "crystal-structure" radius of Li^+ is 0.6A. Around such a small ion six water molecules cannot pack closely into a single spherical shell. Then the six or more water molecules carried by the lithium ion should constitute more than one and less than two spherical shells. The thickness of an "oriented" water molecule is roughly 1.9A. Therefore, the radius of lithium ion should lie between 2.5 and 4.4A; the value given in Table IV is 3.09A.

TABLE III. *Comparison of the equilibrium theory with the conductance data of Shedlovsky[10] and the transference data of Longsworth[13] for* KCl *at 25°.*

M	Λ_{K^+} by (17)	Λ_{Cl^-} by (17)	Λ_{17}	Λ_{exp}	t_{K^+} by (17)	t_{exp}
0.0001	73.06	75.85	148.91	148.90		
0.0002	72.87	75.66	148.53	148.56		
0.0005	72.49	75.28	147.77	147.80		
0.0010	72.08	74.86	146.94	146.93	0.49054	0.4905
0.0020	71.51	74.28	145.79	145.79		
0.0050	70.44	73.19	143.63	143.64		
0.0100	69.31	72.04	141.35	141.32	0.49034	0.4903
0.0200	67.82	70.54	138.36	138.34	0.49017	0.4901
0.0500	65.24	67.92	133.16	133.35	0.48993	0.4899
0.1000	62.80	65.44	128.24	128.90	0.48970	0.4898

[14] See J. R. Partington, reference 11, p. 686.

TABLE IV. *Individual ionic radii in A by the equilibrium theory data from Shedlovsky (reference 10) for conductance and Longsworth (reference 13) for transference at 25°.*

ELECTROLYTES	Λ^0	Λ^0_+	Λ^0_-	$\frac{d\Lambda}{d\mu^{\frac{1}{2}}}$ at $r=0$	r_+	r_{Cl^-}
HCl	426.06	349.73	76.33	−156.5	0.945	1.921
KCl	149.86	73.53	76.33	−96.1	1.978	1.933
NaCl	126.45	50.12	76.33	−90.6	2.562	1.937
LiCl	115.03	38.70	76.33	−88.7	3.095	1.976

APPLICATION OF HYDRODYNAMICS

In the classical approach to conductance problems (theory of electrophoresis) the solvent in which the charged particle is suspended is pictured as a continuous fluid streaming past the particle in very much the same way as it streams along the wall of the tube in which the liquid might be flowing. Actually, hydrodynamic laws based upon such a picture might be expected to break down when the size of the particle is of the same order of magnitude as that of the molecules of the solvent. Eyring[3] in 1936, on the basis of his theory of viscosity, pointed out that the conductances of electrolytes, unless their ions were highly hydrated or for other reasons were large, should be higher than predicted by classical hydrodynamics. More recently, Polissar[15] has discussed the problem and pointed out that values of the ionic radii obtained from their individual equivalent conductances at infinite dilution by the application of classical hydrodynamics should not be expected to be physically valid.

The modern theory has not as yet been worked out to an extent which would make it possible to apply it to ions of such diverse[16] sizes as Li^+ and H_3O^+. Furthermore, for hydronium ion, at least, a new problem arises. Its dimensions, rather than being of the order of magnitude of those of the smallest "diffusing unit" of the solvent, water, are probably considerably smaller. Eyring[3] has calculated from the data of Orr and Butler[17] for the diffusion of light water into heavy water that the "average" dimension $[(\Lambda_1\Lambda_2\Lambda_3)^{\frac{1}{3}}]$ of the diffusing unit is about 3.2A. The thinnest dimension (Λ_1) came out to be 1.47A, a good approximation to the thin dimension of a water molecule; while the other two should be about 4.5A, each. It appears, then, that about four water molecules travel together in the diffusing unit. On this basis, hydronium ion, which has the volume of a single water molecule, should show considerably larger deviations from classical hydrodynamics than the smallest diffusing unit in water. It is suggested, therefore, that the almost "normal" value of the diffusion constant for the self-diffusion of water does not require a

TABLE V. *Comparison of equilibrium theory with experiment*

M	Λ_+	Λ_-	$\Lambda_{(17)}$	Λ_{exp}	t_+	t_{exp}
A. NaCl $\Lambda_+=50.12\left(\frac{1+0.635\mu^{\frac{1}{2}}}{1+1.475\mu^{\frac{1}{2}}}\right)$; $\Lambda_-=76.33\left(\frac{1+0.840\mu^{\frac{1}{2}}}{1+1.475\mu^{\frac{1}{2}}}\right)$						
0.0001	49.71	75.85	125.56	125.56		
.0002	49.54	75.66	125.20	125.21		
.0005	49.21	75.28	124.49	124.50		
.0010	48.85	74.87	123.72	123.72		
.0020	48.36	74.30	122.66	122.67		
.0050	47.42	72.23	120.65	120.58		
.0100	46.45	72.11	118.65	118.43	0.3918	0.3918
.0200	45.19	70.66	115.85	115.65	.3901	.3902
.0500	43.04	68.18	111.22	110.88	.3870	.3876
.1000	41.04	65.88	106.92	106.88	.3838	.3854
B. LiCl $\Lambda_+=38.70\left(\frac{1+0.648\mu^{\frac{1}{2}}}{1+1.663\mu^{\frac{1}{2}}}\right)$; $\Lambda_-=76.33\left(\frac{1+1.015\mu^{\frac{1}{2}}}{1+1.663\mu^{\frac{1}{2}}}\right)$						
0.0004721	37.88	75.30	113.18	113.18		
.0023455	36.94	74.13	111.07	111.04		
.0058846	36.03	72.97	109.00	108.91		
.0100000	35.33	72.09	107.42	—	0.3289	0.3289
.0107787	35.22	71.95	107.17	107.03		
.0199375	34.21	70.67	104.88	104.64		
.0200000	34.20	70.67	104.87	—	.3261	.3261
.0325810	33.25	69.46	102.71	102.34		
.0500000	32.30	68.26	100.57	—	.3212	.3212
.1000000	30.56	66.08	96.64	95.83	.3162	.3168
C. HCl $\Lambda_+=349.73\left(\frac{1+0.630\mu^{\frac{1}{2}}}{1+0.940\mu^{\frac{1}{2}}}\right)$; $\Lambda_-=76.33\left(\frac{1+0.310\mu^{\frac{1}{2}}}{1+0.940\mu^{\frac{1}{2}}}\right)$						
0.0001	348.65	75.85	424.50	424.53		
.0002	348.21	75.65	423.86	423.86		
.0005	347.35	75.27	422.62	422.62		
.0010	346.40	74.86	421.26	421.26		
.0020	345.09	74.26	419.33	419.27		
.0050	342.54	73.14	415.68	415.68		
.0100	339.82	71.93	411.75	411.88	0.8252	0.825_1
.0200	336.20	70.33	406.53	407.12	.8271	$.826_6$
.0500	329.71	67.45	396.15	398.97	.8325	$.829_2$

[15] M. J. Polissar, J. Chem. Phys. **6**, 833 (1938).

[16] Prof. H. Eyring and Dr. E. Gorin in a private communication to the author have informed him that they are at present engaged in investigating the transition from the mechanics for small ions to that for large bodies.

[17] W. J. C. Orr and J. A. V. Butler, J. Chem. Soc. 1273 (1935).

unique mechanism to explain the high conductance of hydronium ion.

Calculation of Conductance from Classical Hydrodynamics[18]

At infinite dilution the mobility, v, of a sphere of radius, r, in a medium of viscosity, η, is given by

$$v = Q/6\pi\eta.$$

Since $v = 300\Lambda/\mathbf{F}$, where v is in e.s.u. and Λ and F are practical units; and since, for all ions to be considered below, the charge Q is equal to $\mathbf{e}$, the electronic charge, it follows that

$$\Lambda^0 = \mathbf{eF}/1800\pi\eta r. \qquad (26)$$

In Table VI values of Λ^0 calculated by means of (26) are given and are compared with the actual values. In the fifth column (②−①) are shown the differences between Λ^0 by (26) and the actual values.

In Fig. 4, log ① and log ② are plotted against the radius. It may be seen from Fig. 4, that, for the largest ion, Li^+, the agreement between the actual conductance and that demanded by classical hydrodynamics is best (within 30 percent); also it may be seen that as the ions become smaller, the agreement becomes progressively worse. Qualitatively, therefore, the results given in Table VI and plotted in Fig. 4 are those that the modern theory of Eyring[3] would predict.

As was mentioned before, the modern theory has not as yet been developed to an extent which would make possible quantitative predictions for ions of such diverse sizes. An empirical approach has been made, however, which can best be justified by the success with which it obtains.

Table VI. *Comparison of Λ^0 at 25° obtained from classical hydrodynamics with the actual values.*

Ion	Radius (A) (Table IV)	Λ^0 classical ①	Λ^0 actual ②	$\Lambda^0_2 = ② - ①$	$A = \Lambda^0_2 r^3$
H_3O^+	0.945	96.2	349.73	253.5	214
Cl^-	1.933	47.04	76.33	29.29	211
K^+	1.978	45.97	73.59	27.62	214
Na^+	2.562	35.49	50.10	14.61	246
Li^+	3.095	29.39	38.70	9.31	276

[18] For a more complete presentation of the theory see H. A. Abramson, reference 6.

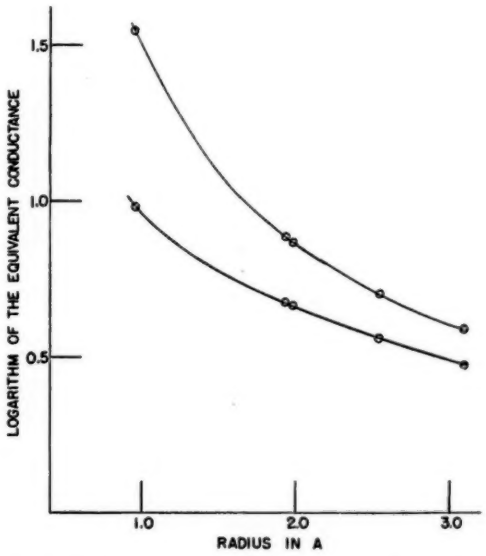

Fig. 4. Comparison of equivalent conductances demanded by classical theory (lower curve) with actual values (upper curve).

For this purpose, two assumptions are made: (1), Λ^0 may be expressed as the sum of two independent conductances

$$\Lambda^0 = \Lambda^0_1 + \Lambda^0_2, \qquad (27)$$

where Λ^0_1 is the contribution demanded by (26) and Λ^0_2 is that demanded by the modern theory; and (2), Λ^0_2 will be approximately inversely proportional to the size of the "hole" which must be created in the liquid in order for the ion to jump from one equilibrium position to another, or, therefore,

$$\Lambda^0_2 = A/r^3, \qquad (28)$$

where A is an undetermined parameter.

From (26), it follows that

$$\Lambda^0 - \mathbf{eF}/6\pi\eta r = A/r^3. \qquad (29)$$

In the fifth column of Table VI, is given Λ^0_2, which was obtained by subtracting the third column from the fourth, while in the sixth column of Table VI is given the parameter, A, obtained by multiplying Λ^0_2 by the cube of the radius. The approximate constancy in A over the 35-fold variation in molecular volume represented in Table VI suggests that the assumptions from which it was calculated may be nearly valid. Whether or not they are found to apply closely as further accurate transference data become avail-

able over a series of temperatures and for other ions, it is felt that two rather definite conclusions may be reached on the basis of the agreement so far obtained: (1), the high conductance of hydronium ion need not be considered anomalous, but rather appears to follow naturally from its small radius; and, (2), the agreement further confirms the physical reality of the ionic radii calculated from the equilibrium theory and, therefore serves to make the theory even more plausible.

ACKNOWLEDGMENT

In conclusion, I should like to express my gratitude to Professor H. A. Abramson of the College of Physicians and Surgeons, Columbia University, for his assistance and interest during the progress of the work and the preparation of the manuscript. I should also like to thank Doctor Theodore Shedlovsky of the Rockefeller Institute, New York, for his kind interest and many valuable suggestions.

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Interpretation of the Mechanism of a Thermal Decomposition from Photochemical Evidence[1]

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By analogy to diatomic molecules it is assumed that if in polyatomic molecules, a transition is permitted between two energy hypersurfaces in a radiative act, it is forbidden in a non-radiative process. The thermal decomposition, in acetaldehyde, yielding methane and carbon monoxide in a unimolecular primary process is shown consequently not to be allowed. However, the bimolecular and the catalyzed processes producing ultimate molecules in the primary act are permitted. The simultaneous occurrence of such a decomposition and a free radical mechanism of a Rice-Herzfeld type adequately account for many of the observations on the catalyzed and high pressure reactions by Hinshelwood and his co-workers, by Verhoek and by Letort.

IT has been shown in a recent paper[2] that there is good reason to believe that acetaldehyde decomposes in its discrete absorption region according to the spontaneous predissociation process

$$CH_3CHO + h\nu \rightarrow CH_3CHO^*, \quad (1)$$

$$CH_3CHO^* \rightarrow CH_4 + CO. \quad (2)$$

The mechanism of the process involves excitation from the normal energy hypersurface to an excited one in which the molecule executes an oscillation. If fluorescence does not occur the molecule eventually rearranges and undergoes a spontaneous predissociation process (decomposes) either, as in the case of formaldehyde,[2] without leaving the excited hypersurface, or by a spontaneous transition to another hypersurface.[2a]

It is the purpose of this paper to indicate how this view of the photochemistry of acetaldehyde clarifies the interpretation of the mechanism of its thermal decomposition.

[1] Paper presented before the Division of Physical and Inorganic Chemistry at the meeting of the American Chemical Society, Baltimore, Maryland, Apr. 6, 1939.

[2] M. Burton and G. K. Rollefson, J. Chem. Phys. **6**, 416 (1938).

[2a] We favor the former view. Acetaldehyde, like formaldehyde, shows a discrete absorption region (indicating a *slow* process) where the decomposition is into CH_4 and CO alone. Inasmuch as the process involved is probably spontaneous (reference 2) it must occur in the same hypersurface for, if an improbable transition to another hypersurface were involved, it should be induced by an external field. Contrary to such an expectation (for an induced process) increase of pressure actually lowers the quantum yield in the photolysis of acetaldehyde at 3130A (P. A. Leighton and F. E. Blacet, J. Am. Chem. Soc. **55**, 1766 (1933)). It should be pointed out, however, that the argument of this paper is independent of any hypothesis as to the mechanism of the spontaneous predissociation.

Location of Hypersurfaces

According to recent calculations[3] the heat of formation of acetaldehyde at 0°K is 555.2 kcal.; of methane, 346.3 kcal.; and of carbon monoxide 209.7 kcal. Assuming that a thermal decomposition

$$CH_3CHO \rightarrow CH_4 + CO \qquad (3)$$

actually does occur in a single step, it is apparent that the products are 0.8 kcal. more stable than the original reactant and that there must be a barrier of some kind to account for the observed stability of acetaldehyde relative to its products.

In Fig. 1 we have made an effort to interpret in a rough way the potential energy relationships involved. In the first place, it must be borne in mind that no two-dimensional representation is adequate. We merely represent cross sections of the hypersurfaces corresponding to certain overall changes.

The dotted curve *A* represents a cross section of the normal hypersurface with varying distance between the carbon atoms (i.e. the curve relative to the products CH_3 and CHO). Actually, other dimensions suffer simultaneous change; for example, the CH_3 group approaches a planar configuration at large values of *r*. It is evident that in such circumstances the representation of potential energy as a function of a single variable is not very precise. However, it is true in a rough sort of way that the dotted curve *A* represents a two-dimensional section of the normal hypersurface corresponding to the products CH_3 and HCO and that the solid curve *A'* represents another section corresponding to the products CH_4 and CO. The value of 93.1 kcal. selected for the heat of dissociation along curve *A* is taken from a recent calculation of bond strengths;[3] it is not essential to the development of our argument. For the potential energy of the system CH_4+CO we adopt the value 138 kcal. given by Henri and his co-workers;[4] Henri has concluded that the normal state of aldehydes and ketones always corresponds to the $a^3\Pi$ state of CO.[5] Here also, it is not essential to our argument that this is the precise state of CO concerned in the normal state of acetaldehyde. It is important, however, that the normal state of CH_3CHO does *not* correspond to the normal state of CO.

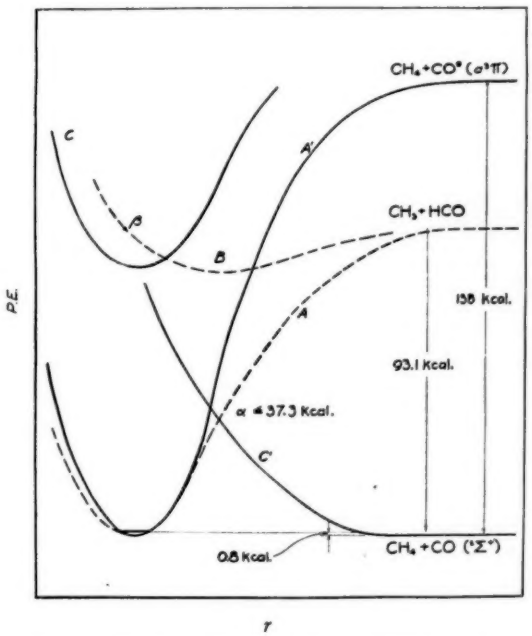

FIG. 1. Schematic representation of potential energy relationships in acetaldehyde.

The first excited state of acetaldehyde is indicated roughly by the two-dimensional section *C*, one region of which lies approximately 81.5 kcal. above the minimum of the normal state.[6] The weakly attractive hypersurface along which decomposition occurs in the diffuse region is represented by the section *B*. Section *B* approaches section *A* asymptotically at a potential energy of 93.1 kcal.[7] The hypersurface **B** intersects the hypersurface **C** in a hyperline one point (at least) of which is at an energy level $\leq$93.1 kcal. In this figure such a point is represented by β, which need not necessarily lie on the particular section *B* as here shown.

The hypersurface **C** may now be further identified by the mechanism recounted in the first paragraph. The hypersurface of the system

[3] M. Burton, J. Chem. Phys. **6**, 818 (1938).
[4] V. Henri, Comptes rendus **199**, 849 (1934).
[5] Cf. V. Henri, Comptes rendus **203**, 67 (1936); R. Cherton, Bull. Soc. Roy. Sci. Liege **12**, 376 (1937); W. A. Noyes, Jr., J. Phys. Chem. **41**, 81 (1937).
[6] The value of 81.5 kcal. is fixed by the wave-length 3484A which is the approximate threshold of ultraviolet absorption in acetaldehyde.
[7] This statement is based on a principle enunciated in reference 3.

CH_4+CO may be a part of hypersurface **C** (as in formaldehyde) or, alternatively, it may be a hypersurface to which a spontaneous transition from **C** is permitted. In a homely sense we may say that CH_4 and CO come down a slope from the valley of hypersurface **C**. In Fig. 1 this repulsive hypersurface for CH_4 and CO is represented by section C' which may or may not be a portion of hypersurface **C**.

It may be seen that the hypersurface **C'** and the normal hypersurface **A** intersect in a hyperline whose minimum height represents the energy of activation for the simple decomposition represented by reaction 3. It must here be emphasized that the intersection of **A** and **C'** represented in Fig. 1 is not necessarily real. The two sections may lie in entirely different planes. However, there is an intersection of the hypersurfaces in a hyperline, represented by the region α; the minimum height of this intersection (relative to the ground level of CH_3CHO) is, for reasons which will appear later, $\leq$37.3 kcal.

Transitions

If we are to accept the conclusions epitomized in Fig. 1, it follows that absorption of radiation causes the transition

$$\mathbf{A}\xrightarrow{h\nu}\mathbf{C}. \qquad (4)$$

We now make an assumption for which we offer no theoretical support. In the case of diatomic molecules the selection rules governing transitions are such that if a transition can occur between two energy states in a radiative act it is forbidden in predissociation, i.e., in a nonradiative process.[8] It is a corollary of this rule for diatomic molecules that if a transition

$$\mathbf{X}\xrightarrow{h\nu}\mathbf{Y}$$

can occur and the transition

$$\mathbf{Y}\rightarrow\mathbf{Y}'$$

can occur spontaneously, then the transitions

$$\mathbf{X}\rightleftarrows\mathbf{Y}'$$

are not allowed in a radiationless act. We will assume that a similar rule (with its corollary) holds for transitions between energy hypersurfaces of polyatomic molecules.

Assuming the validity of the rule just stated, it follows that the adiabatic transition

$$\mathbf{A}\xrightarrow{\alpha}\mathbf{C}' \qquad (5)$$

in the region α is "forbidden." In order for the transition 5 to occur the restraints must be broken down by the presence of an external field. The very important conclusion is that reaction 3 cannot occur in a thermal process. If CH_4 and CO are formed in a primary process it must be in a reaction of the type

$$CH_3CHO+M\rightarrow CH_4+CO+M, \qquad (6)$$

where M may be another molecule or an external field.

Mechanism of Thermal Decomposition

According to the Rice-Herzfeld mechanism[9] the first step in the reaction chain is the decomposition

$$CH_3CHO\rightarrow CH_3+CHO. \qquad (i)$$

This mechanism avoids the difficulty of the anomaly that the reaction with the higher activation energy (*i*) takes place more readily than the one with the lower activation energy (3) by concentrating its attention on the succeeding steps in the free radical chain. These steps

$$CH_3+CH_3CHO\rightarrow CH_4+CH_3CO \qquad (v)$$

$$2CH_3\rightarrow C_2H_6 \qquad (vi)$$

are assumed to be of low activation energy as compared with that of reaction (3).

Using the value $E_i=70$ kcal.[10] and assuming the values (consistent with mechanisms for other reactions) $E_v=15$ kcal. and $E_{vi}=8$ kcal., Rice and Herzfeld obtain a value for the over-all activation energy of the decomposition $\frac{1}{2}(E_i-E_{vi})+E_v=46$ kcal. which may be compared with the experimental value[11] of 45.5 kcal.

[8] Cf. G. K. Rollefson and M. Burton, *Photochemistry and the Mechanism of Chemical Reactions* (Prentice-Hall, New York, 1939), p. 73, where Kronig's rules for diatomic molecules are cited.

[9] F. O. Rice and K. F. Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934).

[10] Based on the mirror experiments of F. O. Rice and W. R. Johnston, J. Am. Chem. Soc. **56**, 214 (1934).

[11] C. N. Hinshelwood and W. K. Hutchison, Proc. Roy. Soc. **A111**, 380 (1926).

The question now arises as to the activation energy of reaction 3 or, properly speaking, reaction 6. Its value may be estimated from some data on the activation energy of the thermal decomposition of acetaldehyde and propionaldehyde both in the pure state and in the presence of suitable catalysts.[11a] According to Hinshelwood and his co-workers[12] the activation energies for both pyrolyses increase as the pressure decreases. Such an effect would be expected, according to the views here presented, under the following conditions:

Two reactions, 6 and *i*, are proceeding simultaneously. The Rice-Herzfeld mechanism, of which the latter is the first step, predicts an over-all reaction of the $\frac{3}{2}$ order, the activation energy of which should not be sensitive to pressure.[13] Increase of pressure, however, would favor reaction 6 relative to *i* with the result that the observed activation energy of the gross reaction would approach more closely to that of reaction 6 with an increase of pressure. Thus, a decrease of activation energy with increase in pressure indicates that the activation energy of process 6 is less than the minimum activation energy observed for the gross reaction; i.e., <45.5 kcal. for acetaldehyde[11] and <56.0 kcal. for propionaldehyde.[12b]

When the free radical mechanism is inhibited by the introduction of means for removal of free radicals, e.g. nitric oxide, it would be expected that the activation energy would also tend toward that of reaction 6. Such a result has been found in the case of propionaldehyde by Staveley and Hinshelwood[12b] who report that the NO inhibited pyrolysis has an activation energy of 58.5 kcal. at 30 mm and of 51.0 kcal. at 350 mm, contrasted with values for the uninhibited reaction of 63.5 and 56.0 kcal., respectively.

Furthermore, reaction 6 is favored by suitable catalysts, e.g., N_2O and NO. Experiments of Verhoek indicate that the N_2O catalyzed pyrolysis of acetaldehyde has an E_6 of 39.8 kcal.[14] and that the NO catalyzed pyrolysis an E_6 of 37.3 kcal.[15]

The mechanism here suggested is supported also in a qualitative way by two investigations of Letort. He reports that the order of the pyrolysis of acetaldehyde varies with the concentration of the products, increasing from 1.5 to 1.8 as the concentration of CO and CH_4 are increased.[16] Inasmuch as the added gases would favor the bimolecular reaction 6 in contrast with the three-halves order chain mechanism, this effect agrees with expectation. Letort also makes the very significant statement[17] in regard to the pyrolysis catalyzed by traces of oxygen that "the temperature coefficient of the additional reaction[18] is negative." From the point of view here presented the simplest interpretation is that the effect detected is relative to the uncatalyzed reaction and that the catalyzed reaction has an energy of activation less than that of the over-all reaction.

[11a] This assumes the energy of activation to be independent of the nature of M. Actually, of course, the function of M cannot be solely to break down the selection rules. M probably produces some perturbation of the energy levels so that the position of the crossing is changed and the chance of "tunneling" is increased. Since both the direction and the magnitude of the first effect is unpredictable the effect of M on the activation energy cannot be predicted.

[12] (a) C. J. M. Fletcher and C. N. Hinshelwood, Proc. Roy. Soc. **A181**, 41 (1933); (b) L. A. K. Staveley and C. N. Hinshelwood, J. Chem. Soc. 812 (1936).

[13] This conclusion seems to be supported experimentally by the work of M. Letort, Comptes rendus **199**, 1617 (1934) who reports that, if only that portion of the CH_3CHO pyrolysis which is of the $\frac{3}{2}$ order be considered, the activation energy at 477° is independent of pressure in the range 50–400 mm.

[14] F. H. Verhoek, Trans. Faraday Soc. **31**, 1527 (1935).

[15] F. H. Verhoek, Trans. Faraday Soc. **31**, 1533 (1935).

[16] M. Letort, Comptes rendus **202**, 491 (1936). It is significant in this connection that the experiments of L. S. Kassel, J. Phys. Chem. **34**, 1166 (1930), conducted over a wide range of pressure, show the thermal decomposition of acetaldehyde to be, not of the three-halves order, but of the five-thirds order.

[17] M. Letort, Comptes rendus **200**, 312 (1935).

[18] The catalyzed reaction.

The Thermal Chlorination of Chloroform

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(Received January 6, 1939)

The thermal chlorination of chloroform has been studied in the range 260–320°C, using chloroform to chlorine ratios from 10 down to $\frac{1}{6}$. For high partial pressures of chloroform the reaction is independent of the chloroform and unimolecular with respect to chlorine. At lower chloroform pressures there is a small dependence on the chloroform in addition to the first-order dependence on chlorine. A mechanism similar to one postulated for the photochemical chlorination of chloroform is discussed and a comparison with the thermal hydrogen-chlorine mechanism leads to the significant conclusion that the reaction has a chain mechanism initiated by chlorine atoms originating on the walls. Production of the latter is interfered with by chloroform adsorption and possibly also by adsorption of reaction products. The chains are broken principally in the gas phase.

THE halogenation of paraffin hydrocarbons has been the subject of considerable research since the halogens are among the few substances with which hydrocarbons react readily. In these researches the chlorination process has received most attention in both the liquid and gaseous phases and under photochemical as well as thermal conditions. Much of the work has been complicated owing to the variety of products produced. It is natural then to examine a simple case first.

The chlorination of chloroform was first investigated photochemically by Schwab and Heyde[2] in carbon tetrachloride solution. Their conclusions on the chain mechanism were criticized by Schumacher and Wolff[3] who showed that the rate of chlorine disappearance was independent of the chloroform concentration and was proportional to the square root of the chlorine concentration accounted for by the following reactions:

$$Cl_2+h\nu\rightarrow 2Cl$$
$$CHCl_3+Cl\rightarrow CCl_3+HCl$$
$$CCl_3+Cl_2\rightarrow CCl_4+Cl$$
$$CCl_3+CCl_3+Cl_2\rightarrow 2CCl_4.$$

There have been no direct measurements of the thermal chlorination of chloroform. From the work of Pease and Walz[4] on methane chlorination, since the rate equations therein found satisfactory, are of the same form as those used by Bodenstein[5] in the hydrogen-chlorine reaction, it would appear that a chain mechanism is involved. Whether the chain mechanism is characteristic of each step in the methane chlorination cannot be judged although the photochemical work would seem so to indicate. The difficulty pointed out by Pease and Walz in connection with the chain mechanism, namely, that the chain length would have to be about 10^{14}, is not so serious as it appears. Using the data given by Giauque and Overstreet[6] on the chlorine atom, chlorine molecule equilibrium, the necessary chain length is found to be more nearly 10^5.

EXPERIMENTAL

The reaction rates were determined by a dynamic method in which mixtures of chlorine and chloroform vapor were allowed to flow through a reaction vessel maintained at constant temperature. The issuing gases were then analyzed for unchanged chlorine and for hydrogen chloride by absorption in potassium iodide solution.

The chlorine used was taken from a tank which had been in use for some time.* It was dried over

[1] (a) Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University, June, 1937. (b) Present address: Mellon Institute, Pittsburgh, Pennsylvania.

[2] G. M. Schwab and U. Heyde, Zeits. f. physik. Chemie **B8**, 147 (1930).

[3] H. J. Schumacher and K. Wolff, Zeits. f. physik. Chemie **B25**, 161 (1934); **B26**, 453 (1934).

[4] R. N. Pease and G. F. Walz, J. Am. Chem. Soc. **53**, 3730 (1931).

[5] See M. Bodenstein and W. Unger, Zeits. f. physik. Chemie **B11**, 253 (1931).

[6] W. F. Giauque and R. Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).

* Following Pease and Walz' suggestion that prior use rids the gas of its dissolved impurities, principally oxygen,

calcium chloride and passed to a flowmeter by way of a three-liter flask. The latter in conjunction with an overflow bubbler containing 50–60 cm chloroform served to give a constant flow of gas. The flowmeter was of the type described by Benton[7] using carbon tetrachloride as manometer fluid. The rate of flow was regulated in the early part of the work by a steel valve. This was later replaced with advantage by an all-glass greaseless valve of the Bodenstein type using a silver chloride seat. The flowmeter calibration was made by direct absorption of chlorine in potassium iodide solution and subsequent titration of the iodine liberated with sodium thiosulphate solution.

The chloroform used was first thoroughly washed with water, dried over fresh calcium oxide and distilled three times under nitrogen. A quicklime treatment was made after each distillation, the middle fraction being taken each time. The sample for use was introduced into a reservoir maintained by thermostatic control at constant temperature (80°C), the vapors passing through a graphite lubricated stopcock to a flowmeter using mercury as the manometer fluid. Calibration of the flowmeter was made by collecting the chloroform delivered under given conditions and weighing. Condensation of the chloroform vapor during its passage from the reservoir to the furnace was prevented by maintaining all connecting tubes including the flowmeter at 90°C.

The use of separate flowmeters for each constituent was adopted after preliminary work had shown that chlorine could not easily be used as a carrier gas for the chloroform vapor owing to the high solubility of chlorine in chloroform. During an experiment the amount of chlorine liberated from solution by the chloroform which had been vaporized was considerable and measurably altered the composition of the mixture.

The reaction vessel for the major portion of the work was a *U*-tube made from 1.67-cm inside diameter Pyrex tubing of 40.2 cm total length and 211 sq. cm area. The connecting tubes were of 1-mm bore capillary. The total volume within the furnace was 87.10 cc giving a surface-volume ratio of 2.42.

The runs using increased surface were made in a vessel constructed of 0.25-cm inside diameter tubing, 11.88 meters in length affording a surface of 934 sq. cm and a volume of 62.8 cc. The surface-volume ratio was thus 15. A second such vessel of 27.8 cc capacity and surface-volume ratio of 15.4 was used in some experiments.

The furnace was a Nichrome resistance furnace of the conventional type with a metal interior to reduce temperature gradients. Temperatures were measured by a platinum resistance thermometer, manual control of the furnace regulating the temperature to ± 0.2°C.

The exit tube from the reaction vessel, also maintained at 90°C, carried a ground glass joint which fitted the absorption tube constructed from 1.8-cm inside diameter tubing, 16 cm long, in such a way that the vapors passed over, rather than bubbled through, the potassium iodide solution. Experiment showed that under such conditions absorption was complete. The potassium iodide solution contained about 90 g per liter. The iodine liberated was titrated with 0.1*N* sodium thiosulphate and following this the acid titration used 0.05*N* sodium hydroxide. The usual starch indicator was used for the former and bromthymol blue for the latter.

The arrangement of the apparatus is shown schematically in Fig. 1. The diagram includes the disposition of the apparatus for the study of the effects of nitrogen, oxygen, hydrogen chloride and carbon tetrachloride. The hydrogen chloride flowmeter contained concentrated sulphuric acid as manometer fluid while that for the carbon tetrachloride used mercury.

Results

Because of the large number of experiments made, it will suffice that some illustrative runs are detailed and the over-all data tabulated. In Table I data are given for some typical runs which are self explanatory. It should be realized that the extent of reaction may be calculated from both the thiosulphate and from the alkali titer. It was found that somewhat more concordant results were obtained using the thiosulphate titer. Consequently all results are so expressed. The lower row of figures for percentage chlorine reacted in Table I was calculated on the basis of

no further purification was made. The results obtained were consistent over many months operation.

[7] A. F. Benton, Ind. Eng. Chem. **11**, 623 (1919).

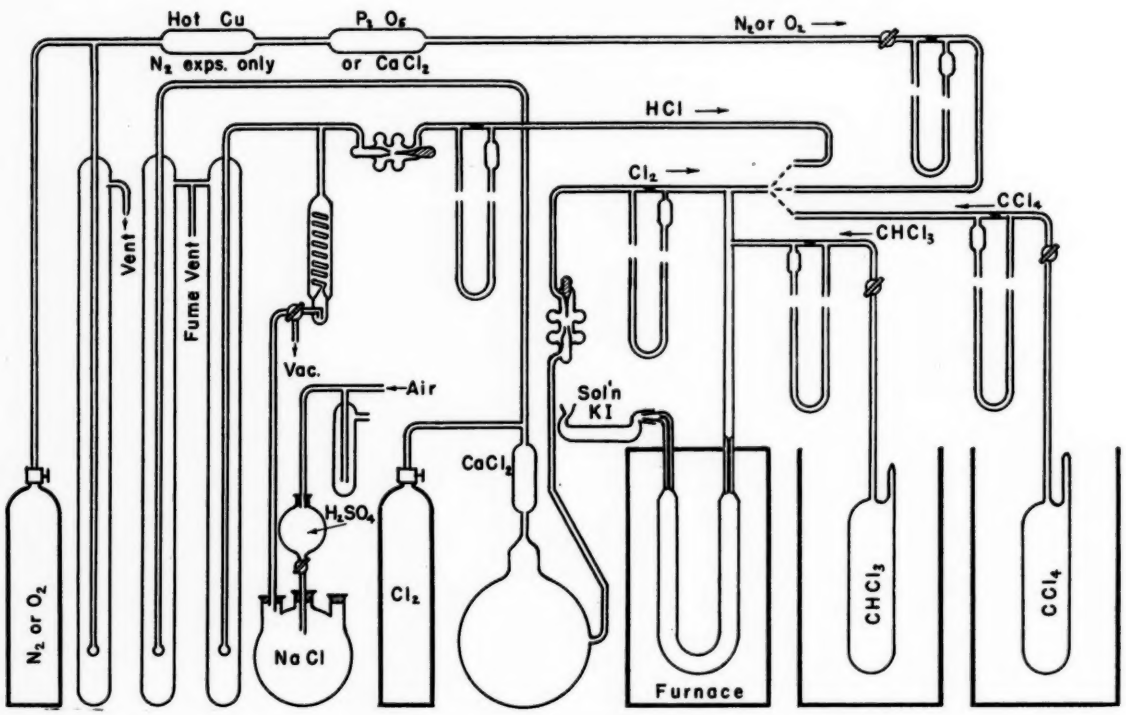

FIG. 1. Apparatus.

the alkali titration. All other figures are based on the thiosulphate titration.

The time of contact was taken as the ratio of the volume of the reaction flask to the rate of flow of the gases. This assumes, first that the gases are thoroughly mixed before entering the heated zone and second, that the gases pass through the flask without further mixing by diffusion or convection. That this latter condition holds is indicated by the following calculation of the extent of diffusion using the relation given by Langmuir[8] for such circumstances. In an extreme case with 50 percent reaction at 320°C, for a stream velocity of 4 to 8 cm per sec. through the reaction zone 40 cm in length, taking an extreme diffusion coefficient of 0.2 cm² per sec. at 0°C the correction due to diffusion becomes

$$\frac{nD}{sL}\log\frac{a}{c_0}=\frac{n\times 0.2\times 600^2/273^2}{4\times 40}\times 0.3$$

$$=1.8\times 10^{-3}n$$

which, for n slightly greater than unity, is considerably less than one-tenth of one percent. In the increased surface experiments the stream velocity is so high due to the smaller diameter tubing that diffusion could not possibly enter.

The complete data obtained for the runs involving chloroform and chlorine alone are given in Table II.

A cursory examination of the above results seemed to indicate that the reaction rate was much more dependent on the chlorine than on the chloroform. Assuming the rate to be first order with respect to chlorine and independent of the chloroform, the velocity constants so calculated are approximately constant at 531°K but at the higher temperatures show marked trends. The trends at each temperature however are less marked, the higher the partial pressures of chloroform, indicating that the reaction approaches first order in presence of an excess of chloroform. At lower partial pressures of chloroform the unimolecular constants should apparently be corrected by dividing by a factor of the type $(1+K/CHCl_3)$ such that for high pressures of chloroform the term would vanish. On closer analysis it was found that K in this expres-

[8] I. Langmuir, J. Am. Chem. Soc. 30, 1742 (1905). See p. 1754 for meaning of symbols.

sion was itself a function of the extent of reaction. After considering numerous possibilities it was found that the concentration of hydrogen chloride or its equivalent, the concentration of carbon tetrachloride produced by the reaction, could be used most adequately to represent K. The overall rate equation thus becomes:

$$-\frac{d(Cl_2)}{dt}=\frac{K_1(Cl_2)}{1+K_2(CCl_4)/(CHCl_3)}.$$

Letting a be the initial concentration of chloroform, b, that of chlorine and x, the concentration of hydrogen chloride or carbon tetrachloride at time t, it follows that:

$$\frac{dx}{dt}=\frac{K_1(b-x)}{1+K_2x/(a-x)},$$

which on integration yields

$$\log\frac{b}{b-x}+\frac{K_2b}{a-b}\log\frac{b}{b-x}+\frac{K_2a}{b-a}\log\frac{a}{a-x}=\frac{K_1t}{2.303}$$

or, when $a=b$,

$$2.303(1-K_2)\log\frac{b}{b-x}+\frac{K_2x}{b-x}=K_1t.$$

The evaluation of K_1 and K_2 was made by setting up an equation for each run of the type $mK_1=nK_2+p$. The series of simultaneous equations treating m, n and p as constants and K_1 and K_2 as variables was then solved graphically.* The results obtained are given in Table III together with the mean deviations. To demonstrate how closely these constants can reproduce the experimental observations, the percentage chlorine reacting for the particular times of contact used in the experiments was calculated and is included in Table II to facilitate direct comparison with the observed values. The agreement at the two intermediate temperatures is really excellent though not quite so good at the lowest and highest temperatures. Under these conditions however the experimental accuracy is not as high since at low temperatures the amount of reaction is small and the analytical procedure necessitates taking a small difference between two large titers; at high temperatures the reaction is almost complete, the chlorine leaving the furnace in but small amounts. It is significant that there is no marked trend in the differences between the observed and calculated values and it may be added the agreement is considerably better than that obtained using several other empirical rate expressions.

* This involved plotting the data for each run as a graph of K_1 against K_2. Theoretically these lines should all intersect at a point whose value would be (K_1, K_2). Experimental error causes numerous intersections. All intersections were averaged, save, for example, where two lines were almost coincident and a slight error in either would make an enormous change in the coordinates of the intersection (K_1, K_2), or where the data for a particular run is so at variance with other data at the same temperature that the data were completely omitted.

Effect of surface

It may be remarked at the outset, that it was found necessary during the course of the work, to run the reaction mixture through the furnace for some time before steady results could be obtained, particularly after any change in the system, or even in the mixture, had been made. This would suggest a conditioning of the surface. After such a lapse of time however, steady values were always obtained and could be reproduced weeks later. The data obtained in the presence of increased surface are given in Table IV. The surface-volume ratio was increased from 2.4 to

TABLE I.

Run Number	51	B1	S-16 Increased Surface
Temperature °K	563	575	575
Moles $CHCl_3$ entering per min.$\times 10^4$	1.955	2.250	2.860
Moles Cl_2 entering per min.$\times 10^4$	1.945	2.610	0.475
Moles HCl entering per min.$\times 10^4$	—	2.250	—
Initial pressure $CHCl_3$ min. Hg	378	239	647.5
Initial pressure Cl_2 min. Hg	376	278	107.5
Initial pressure HCl min. Hg	—	239	—
Contact time min.	4.796	2.58	1.755
Normality Thio.	0.09156	0.09133	0.09144
Normality NaOH	0.0525	0.09732	0.09731
cc Thio. per min.	2.398	3.431	0.601
cc NaOH per min.	1.617	3.375	0.205
Moles $CHCl_3$ leaving per min.$\times 10^4$	1.109	1.206	2.660
Moles Cl_2 leaving per min.$\times 10^4$	1.099	1.566	0.275
Moles HCl leaving per min.$\times 10^4$	0.846	3.294	0.200
Moles CCl_4 leaving per min.$\times 10^4$	0.846	1.044	0.200
% Cl_2 reacted	43.4 43.6	40.0 39.7	42.10 42.00

TABLE II.

Initial part. press. mm Hg $CHCl_3$	Cl_2	Ratio $CHCl_3/Cl_2$	Contact Time Min.	$\%Cl_2$ Reacted	$\%Cl_2$ (Calc'd)
Temperature 531°K					
697	68	10/1	2.96	7.0	11.2
698	68	10/1	3.98	10.7	14.7
671	83	8/1	3.49	12.6	12.9
668	93	7/1	5.98	21.2	20.7
658	103	6.4/1	4.63	18.4	16.6
648	105	6/1	2.81	10.2	10.5
552	187	3/1	7.68	22.2	24.7
551	185	3/1	4.12	16.4	14.7
553	185	3/1	2.48	9.6	10.8
574	185	3/1	3.23	10.5	11.6
376	383	1/1	8.75	26.0	23.6
379	379	1/1	5.03	19.3	16.3
375	378	1/1	3.67	13.3	12.0
379	374	1/1	4.06	14.7	13.2
189	566	1/3	8.07	16.3	15.8
189	566	1/3	4.76	11.1	12.0
192	576	1/3	5.86	13.7	13.7
109	649	1/6	6.17	11.1	10.6
110	649	1/6	8.15	14.0	12.0
Temperature 563°K					
697	66	10/1	3.88	49.9	48.5
693	72	10/1	2.83	37.9	38.0
659	109	6/1	4.51	52.4	52.5
660	110	6/1	3.30	41.3	42.2
654	108	6/1	2.75	37.3	36.9
567	195	3/1	5.13	54.7	54.2
566	188	3/1	2.30	30.9	31.0
571	192	3/1	3.36	41.5	41.2
572	192	3/1	2.79	35.8	36.0
371	388	1/1	9.58	65.3	59.7
378	377	1/1	5.51	48.8	47.3
362	388	1/1	3.68	37.7	37.0
377	375	1/1	3.29	35.9	35.0
378	376	1/1	4.80	43.4	44.0
194	558	1/3	5.40	34.4	28.6
188	564	1/3	4.49	31.6	27.0
Temperature 575°K					
657	105	6/1	3.70	69.1	69.4
654	106	6/1	2.47	55.5	55.2
653	108	6/1	2.02	49.2	49.0
571	192	3/1	3.44	64.5	63.5
569	191	3/1	2.24	50.0	50.0
568	192	3/1	1.76	41.3	42.5
383	380	1/1	4.95	60.4	59.9
379	379	1/1	4.24	56.5	56.3
378	381	1/1	3.32	48.0	50.8
Temperature 593°K					
706	71	10/1	2.17	81.7	80.0
704	71	10/1	2.02	78.8	77.3
668	109	6/1	3.47	91.7	91.3
666	109	6/1	2.40	82.0	82.0
667	110	6/1	1.79	73.4	72.5
563	190	3/1	4.86	94.3	95.2
568	195	3/1	3.22	85.3	87.5
569	191	3/1	2.02	73.2	74.3
569	191	3/1	1.55	65.2	65.8
381	383	1/1	4.48	82.2	79.8
380	382	1/1	3.73	75.6	76.4
381	381	1/1	3.15	74.8	73.2
381	381	1/1	2.93	68.9	71.6

15.1, that is, by a factor of 6.3. The last column gives the percent chlorine that would have reacted in the reaction vessel of lower surface-volume ratio as calculated from the constants in Table III. There appears to be a small but systematic increase in the rate on the increased surface. If it were justifiable to assume that the reaction was partly homogeneous and partly heterogeneous, each distinct from the other, the heterogeneous portion would be less than ten percent of the whole. The surface effect is discussed later.

Inert gas effect

The effect of adding nitrogen, carbon tetrachloride and hydrogen chloride to the chloroform-chlorine mixture is summarized in Table V. All three gases have substantially the same effect at corresponding concentrations; namely, a moderate depressing effect, obvious at the three higher temperatures but unquestionably also present at the lowest temperature though masked by the large experimental error. At 563°K where most data are available it would seem that carbon tetrachloride has a slightly greater depressing effect than hydrogen chloride and this in turn greater than nitrogen. At 575° the effect of carbon tetrachloride is also greater than that of hydrogen chloride.

Effect of oxygen

For comparison with the chlorination reactions the effect of added oxygen was determined. In preliminary experiments it was found that mixtures of chloroform and oxygen at 575°K gave no free chlorine and only traces of acid were produced. Furthermore, after the runs with chloroform, chlorine and oxygen, the oxygen could be recovered almost quantitatively by absorption in pyrogallol even after a preliminary washing with alkali to remove any phosgene which might be produced. The reaction does not therefore involve any considerable oxidation of the chloroform. Nevertheless after a number of runs had been

TABLE III.

T°K	K_1(min.$^{-1}$)	K_2
531	0.040±0.002	1.90±0.30
563	0.175±0.004	1.31±0.23
575	0.352±0.008	1.42±0.08
593	0.77 ±0.02	0.77±0.03

made a small amount of a white crystalline solid condensed in the exit tube from the furnace. The amount was too small to be characterized definitely but had an odor of hexachlorethane. This might suggest a possible oxidation of chloroform to trichlormethyl radicals which subsequently polymerized. The extent of this in a single run must have been very small. Despite this however, oxygen has a marked effect on the chlorine consumption as is seen from Table VI. The experiments are too few to permit any quantitative conclusions being drawn. The increase in the chlorination by even small amounts of oxygen, in notable contrast to the inhibition by oxygen found in the hydrogen-chlorine or methane-chlorine reactions, is significant and worthy of further study.

Temperature coefficient

When the logarithms of K_1 (given in Table III) are plotted in the conventional way against the reciprocal of the absolute temperature, the points at 531,575 and 593°K lie on a straight line whose slope corresponds to an energy of activation of 29,700 cal. The point at 563°K lies below the line and the average deviation at this temperature is not sufficient to account for the departure. The energy of activation corresponding to K_1 is thus taken as 30 kcal.

The variation with temperature of the values of K_2 given in Table III, does not seem to follow any definite law. Too much reliance however, cannot be placed on these values. The algebraic treatment necessary to their evaluation would demand a very high order of accuracy in the original observations. At 531° only six intersections could be used to determine K_2; at 563° and at 575°, twelve intersections were averaged, while at 593° only eight appeared to have sufficient precision. Statistically, the two intermediate temperatures give the more reliable values thus showing a small increase in K_2 with increase in temperature.

TABLE IV. *Increased surface.*

Initial part. press. mm Hg $CHCl_3$	Cl_2	Ratio $CHCl_3/Cl_2$	Contact Time Min.	%Cl_2 Reacted	%Cl_2 (Calc'd)
Temperature 593°K					
370	383	1/1	4.72	87.7	80.7
376	377	1/1	2.46	73.8	68.0
376	377	1/1	0.99	47.1	44.8
Temperature 575°K					
648	108	6/1	1.76	42.1	44.0
379	381	1/1	3.13	59.3	49.4
380	381	1/1	1.72	43.5	35.5
381	381	1/1	0.96	27.6	24.0
Temperature 563°K					
647	108	6/1	1.80	27.2	26.4
379	381	1/1	3.16	40.9	34.1
380	381	1/1	1.35	20.9	18.5
380	381	1/1	1.02	16.6	14.5
Temperature 531°K					
374	382	1/1	6.62	17.3	19.3
377	382	1/1	3.98	11.3	12.9
379	380	1/1	1.18	4.7	4.2

TABLE V.

Added Gas X	T°K	$CHCl_3/Cl_2/X$	Contact Time Min.	%Cl_2 (Obs)	%Cl_2 (Calc'd)
CCl_4	531	1 : 1 : 1	2.95	10.7	10.0
	531	0.3 : 1 : 1.1	3.30	6.6	9.5
	531	3.3 : 1 : 3.5	3.12	10.4	11.3
	563	1 : 1 : 1	2.33	21.6	28.0
	563	1 : 1 : 1	4.29	36.0	41.3
	563	1 : 1 : 1	3.01	29.0	33.0
	563	0.9 : 1 : 1.2	2.85	28.3	31.4
	563	0.3 : 1 : 1	3.08	19.8	23.0
	575	1 : 1 : 1	2.14	34.5	40.5
	575	1 : 1 : 1	4.17	50.1	56.0
	575	1 : 1 : 1	2.71	41.9	46.0
	575	1.2 : 1 : 1.7	2.80	37.1	48.3
	575	0.4 : 1 : 1	2.67	30.9	32.6
	593	1 : 1 : 1.2	3.08	69.0	72.5
	593	1.9 : 1 : 1.9	2.68	72.2	79.5
	593	1 : 1 : 1	2.26	60.2	66.2
HCl	531	2.4 : 1 : 1.8	3.28	14.7	10.5
	531	0.5 : 1 : 0.8	3.11	6.8	9.6
	563	1 : 1 : 1	3.30	30.3	35.0
	563	1 : 1 : 1	6.55	45.7	51.2
	563	1 : 1 : 1	3.97	34.8	39.5
	563	4.7 : 1 : 0.7	3.03	22.1	39.5
	563	3.1 : 1 : 2.2	3.09	37.6	39.0
	575	1 : 1 : 1	6.45	66.5	65.8
	575	1 : 1 : 1	2.86	43.6	47.5
	575	1 : 1 : 1	3.65	50.5	53.0
	575	0.9 : 1 : 0.9	2.58	40.0	43.3
	575	0.3 : 1 : 0.7	3.00	22.0	28.6
	593	0.9 : 1 : 0.6	2.62	53.9	65.5
	593	0.7 : 1 : 0.7	2.75	44.6	58.5
N_2	563	1 : 1 : 1	2.92	28.0	32.3
	563	1 : 1 : 1	2.34	24.7	28.0
	563	1 : 1 : 1	4.52	38.7	42.5
	575	1 : 1 : 1	2.24	33.9	41.7
	575	1 : 1 : 1	2.67	43.0	45.7
	575	1 : 1 : 1	3.55	51.4	52.4
	575	3 : 1 : 1	2.35	50.5	51.2

TABLE VI.

T°K	$CHCl_3/Cl_2/O_2$	CONTACT TIME	%Cl_2 REACTED	%Cl_2 CALC'D
563	1 : 1 : 1	3.06	83.1	33.4
575	1 : 1 : 0.1	3.22	61.0	50.0
575	1 : 1 : 1	2.99	84.8	48.4
575	1 : 1 : 1	2.38	81.5	43.3
575	1 : 1 : 1	2.36	79.6	43.0

Mechanism

In the studies of the photochemical chlorination of chloroform by Schwab and Heyde and by Schumacher and Wolff, the formation of carbon tetrachloride and hydrogen chloride is considered to proceed according to the reactions:

$$Cl_2+h\nu\rightarrow 2Cl$$
$$Cl+CHCl_3\rightarrow CCl_3+HCl$$
$$CCl_3+Cl_2\rightarrow CCl_4+Cl.$$

Schwab and Heyde consider the second reaction to be reversible and that chains end by a recombination of chlorine atoms. Schumacher and Wolff, unable to find any inhibition by hydrogen chloride, consider the above reactions only, terminated by:

$$2CCl_3+Cl_2\rightarrow 2CCl_4.$$

Although chain-breaking reactions are frequently postulated as involving three-body collisions or associations on a wall, a strictly third-order reaction is somewhat unusual. To account for the observed kinetics, however, atom or radical associations were ruled out, especially since no C_2Cl_6 was found even after many experiments. By assuming that the chain propagating reaction between CCl_3 and Cl_2 has an energy of activation of 8 kcal., Schumacher and Wolff show that the infrequency of the third-order chain breaking step, even requiring no activation, will not lead to abnormally large quantum yields. It may be remarked that in this work only short periods of illumination were used, corresponding to small total amounts of reaction. Furthermore the relatively low temperature, 50–70°C, would lead to a simplicity not to be expected in the thermal reaction.

By eliminating numerous other possible mechanisms as unsatisfactory, the following series of reactions is proposed as the general course of the thermal reaction. While not entirely satisfactory, due probably to an over-simplification, it appears to account for most of the observations.

$$Cl_2\xrightarrow{1}2Cl,$$
$$Cl+CHCl_3\underset{6}{\overset{2}{\rightleftarrows}}CCl_3+HCl,$$
$$CCl_3+Cl_2\underset{5}{\overset{3}{\rightleftarrows}}CCl_4+Cl,$$
$$2CCl_3+Cl_2\xrightarrow{4}2CCl_4.$$

Recent thermochemical data give a value of about 13 kcal. as the heat of reaction 2. Taking the energy of activation given by Schumacher and Wolff as 4.3, that for the reverse reaction 6 will be about 17 kcal. The reaction should be easily possible in our temperature range. Similarly reaction 5 may be shown to require an activation energy of the order of 20 kcal. The steady-state concentrations are then given by:

$$[Cl]=\frac{2k_1+k_3(k_1/k_4)^{\frac{1}{2}}[Cl_2]+k_6(k_1/k_4)^{\frac{1}{2}}[HCl]}{k_2[CHCl_3]+k_5[CCl_4]},$$

$$[CCl_3]=(k_1/k_4)^{\frac{1}{2}}.$$

Hence

$$\frac{d[HCl]}{dt}=\frac{k_2(2k_1+k_3(k_1/k_4)^{\frac{1}{2}})[Cl_2][CHCl_3]+k_2k_6(k_1/k_4)^{\frac{1}{2}}[HCl][CHCl_3]-k_6(k_1/k_4)^{\frac{1}{2}}[HCl]}{k_2[CHCl_3]+k_5[CCl_4]}.$$

Since evidently $k_4\gg k_1$, expressions involving their ratio may be neglected, giving:

$$\frac{d[HCl]}{dt}=\frac{2k_1[Cl_2]}{1+k_5[CCl_4]/k_2[CHCl_3]},$$

an equation of the form found to fit the experimental data when K_1 is equal to $2k_1$ and K_2 is k_5/k_2.

The observed energy of activation, 30 kcal, derived from K_1 is much lower than the heat of dissociation of Cl_2 into atoms. Christiansen,[9] however, has suggested that this dissociation must be a wall reaction in the thermal hydrogen-

[9] J. A. Christiansen, Zeits. f. physik. Chemie **B2**, 405 (1929). See also J. C. Morris and R. N. Pease, J. Am. Chem. Soc. **61**, 391, 396 (1939).

chlorine combination with an activation energy of 25–30 kcal. to account for the observed rate. It is assumed then, that chains are initiated on the walls. The experiments in presence of an increased surface do show an increase in rate. However, the increase in surface, by a factor of 6.2, was obtained by using tubing with a smaller diameter, decreased that is, from 1.67 cm to 0.25 cm; a factor of 6.7. Now if the chains were broken entirely on the walls one would expect the chain breaking efficiency to be increased by this decrease in diameter by a factor of 6.7^2, or approximately 45, which might obscure an increase in K_1 as the surface increased. That K_1 does increase at all would suggest that chain breaking occurs chiefly in the gas phase, pointing to a reaction such as 4. The effect of added gases is also in agreement with this view, since diffusion of the chain carrier into the gas phase would be hindered thereby. It is somewhat surprising that the effects of added amounts of the reaction products, carbon tetrachloride and hydrogen chloride, are not more marked than actually observed, in view of the postulated reactions 5 and 6, though as already pointed out, carbon tetrachloride and hydrogen chloride do seem slightly more effective than nitrogen.

Although the above reaction scheme thus appears plausible it is evident that there must be complicating factors. In comparing the data obtained here with those for the thermal hydrogen-chlorine combination the first point of difference to be noted is the temperature at which measurable rates are obtained; 200°C in the hydrogen-chlorine reaction, 300° for chloroform-chlorine. This is significant if the mechanisms for the two reactions are compared. The initial step is the same for both. This is succeeded in one case by reaction between a chlorine atom and a hydrogen molecule, involving 6 kcal. energy of activation, in the other, by reaction between a chlorine atom and chloroform, involving about 4 kcal. In view of this similarity, the necessity for the much higher temperature for chloroform-chlorine must mean some interference by the chloroform with chlorine atom production; probably by an adsorption of chloroform. This is in agreement with the observation that at high partial pressures of chloroform the rate is almost independent of the chloroform. It is almost impossible to predict what effect the reaction products, or added gases, may have on this adsorption and hence useless to discuss in any detail further, their net effect on the reaction rate. It is interesting to note that if the reaction were entirely heterogeneous involving a simple displacement of adsorption by carbon tetrachloride, the rate expression, assuming weak adsorption of chlorine would be:

$$\frac{dx}{dt}=\frac{k_1[Cl_2][CHCl_3]}{1+k_2[CHCl_3]+k_3[CCl_4]}$$

which, neglecting unity in the denominator and dividing numerator and denominator by k_2 $[CHCl_3]$, would yield a rate equation of the type found to express the observed data. The effect of increased surface on the rate is not, however, in accord with a completely heterogeneous reaction. Nevertheless it is inevitable from this point of view that the suggested scheme of reactions is oversimplified from what actually occurs. Thus, in conclusion, to equate the experimental K_2 directly with the theoretical k_5/k_2 may not be justified. From Schumacher's data k_5/k_2 should correspond to a small positive energy of activation, whereas, discounting the error in the evaluation of K_2 already noted the general trend is a decrease with increase of temperature. If carbon tetrachloride were adsorbed, or at least modified the chloroform adsorption, then its presence would affect not only reaction 5 as in the scheme, but indirectly, reaction 1 and therefore also all the others. Hence since the apparent energy of activation in a completely heterogeneous reaction is less than the true value by the heat of adsorption, the possibility exists of reducing the already small energy corresponding to k_5/k_2 to an apparent negative value.

Optical Sensitizing of Silver Halides by Dyes

II. The Mechanism of Optical Sensitizing and the Quantum Equivalent*

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The photolysis of silver bromide sensitized with certain acid and basic dyes has been followed by chemical and photometric determination of the silver produced. It was found that in the absence of halogen acceptors the dye is progressively bleached, but in the presence of halogen acceptors it is recovered chemically unchanged. However, the dye actually combines with the bromine released but is regenerated on giving up the bromine to another less active acceptor. The maximum of sensitivity is found to occur considerably before adsorption-saturation, and at about the same adsorption-density for both photolysis and photographic sensitivity. The apparent desensitizing action of sensitizing dyes at higher adsorption-densities is ascribed to the facility of rebromination by the dye:bromine addition compound.

So long as the photographic yield is proportional to the adsorption-density of the dye an initial quantum equivalent of unity is found—one quantum of light absorbed by the dye produces one silver atom. In regard to the mechanism of sensitizing, photovoltaic experiments indicate the release of photoconductance electrons. These may be emitted either by the adsorbed dye itself or by bromide ions of the silver bromide receiving energy from the photoactivated dye. Some indirect evidence supports the latter view.

IN a preceding paper[1] the nature of the adsorption of sensitizing dyes to silver halides was discussed, and certain conclusions reached as to the orientation of the dye molecules attached to the surface. We desire now to report some investigations of the photolysis of the optically sensitized silver halides. It is true that conclusions reached for directly measurable reactions in light may not be entirely applicable to the phenomena of the "latent image," which are indirectly revealed by development. However, recent optical methods[2] have made it possible to measure in certain cases the "invisible" or latent image, and the basic identity of the processes involved may be regarded as reasonably certain. One of the first things to be determined for the photolysis is whether the dye molecule is destroyed in the course of facilitating the decomposition of silver halide, as postulated by certain chemical theories[3] or whether it is conserved unchanged, as supposed by other physical theories.[3] The observation of Lescynski[4] that some twenty or more atoms of silver could be obtained (for a certain exposure) per dye molecule present indicated that either a "physical" transfer of energy is effected, or else a chain reaction with regeneration of the dye molecule. Recently Bokinik and Iljina[5] have published results to somewhat the same effect. Working with silver bromide sols sensitized with erythrosine, they observed an initially linear formation of silver atoms with increasing number of erythrosine molecules added to the sol, and, according to the exposure, yields of four to fifteen atoms of silver per dye molecule.

The present investigation deals with three problems:

a. The persistence of the optically sensitizing dye molecules during photolysis,

b. the relation of the amount of photolysis, in terms of silver atoms formed, to the number of dye molecules adsorbed per unit area, i.e., to the percentage saturation,

c. the relation of the number of silver atoms formed to quanta of light absorbed by the dye, hence, the quantum equivalent of the absorbed radiation.

It is evident that a *sine qua non* for these investigations is a reliable and sensitive method for the determination of very small amounts of metallic silver. We shall discuss the details of the

* Communication No. 719 from the Kodak Research Laboratories.

[1] S. E. Sheppard, R. H. Lambert and R. D. Walker, J. Chem. Phys. **7**, 256 (1939).

[2] A. van Kreveld, and H. J. Jurriëns, Physica, [IV] **4**, 297 (1937).

[3] Cf. references in review by G. Kornfeld, "The Action of Optical Sensitizers on the Photographic Plate," J. Phys. Chem. **42**, 795 (1938).

[4] W. Lescynski, Zeits. wiss. Phot. **24**, 261 (1926).

[5] J. I. Bokinik and Z. A. Iljina, Acta Physicochim., U. R. S. S. **3**, 383 (1935).

analytical methods in another place, merely summarizing [our conclusions] here and indicating the method finally adopted and its limitations. After preliminary experiences with the methods of iodization, followed by back titration with arsenite[5] and with electrometric titration with 0.001 molar solution, according to Lühr and Weigert,[6] we finally adopted a photometric method, similar in some respects to that of van Kreveld and Jurriëns[2] but calibrated on the direct chemical analysis. Measurements were made in both cases with a photronic cell photometer, but whereas van Kreveld and Jurriëns measured the opacity of the photolytic silver directly,* in a dry plate or film, we measured it after solution of the silver halide in a thiosulfate-sulfite fixing bath. The latter procedure has the disadvantage that some oxidation, and solution, hence loss, of silver, is liable to occur, but we found that if the photometric measurements were made within 15 minutes the loss was negligible for the quantities concerned. These amounts of silver were considerably above those in the "latent image" region, for which the van Kreveld and Jurriëns procedure is probably preferable, and experiments are in progress to adapt it to our problem.

An uncertainty which presents itself with the photometric method is the dependence of the optical density upon the dispersity or particle size of the silver. In the procedure which we employed, it appeared possible that the dispersity of the silver produced in suspension after solution of the silver halides might depend upon the original dispersity or grain size of the silver halide. Comparative chemical and photometric determinations were made of two outstandingly different systems: (a) a silver bromide sol of ultramicroscopic particles, (b) a relatively coarse grained (negative) silver bromide emulsion.

The resultant measurements showed that (i) the optical density, $D=\log_{10} I_0/I$, where I_0 = incident, I = transmitted intensity, is directly proportional to the mass of silver (ii) the proportionality constant, or photometric constant, is the same in both cases.† It may be assumed, therefore, that on solution of the silver halide (and gelatin, when present) in the fixing solution, silver sols of substantially the same mean particle size are produced. This constancy might not obtain for the colloid silver particles originally present as formed in the silver halide grains, although in *any particular emulsion* van Kreveld and Jurriën's measurements indicate that for low orders of exposure the mass of silver is proportional to the optical density.

Photolysis of Dye Sensitized Silver Bromide

The question of the persistence of the dye molecules during photolysis was examined as follows. Silver bromide sols were prepared similar to those used by Bokinik and Iljina. They were prepared by adding simultaneously 50 cc of 0.4 N $AgNO_3$ aq. and 50 cc of 0.404 N KBr aq. to 800 cc of water. The delivery pipettes each had a time of flow of 45 seconds, and the solution was stirred mechanically during the addition. Thereafter 50 cc of a "buffer" solution, giving a 0.02 molar strength, were added. Bokinik and Iljina used phosphate buffers, but after some experiments with these, and also with barbituric acid (veronal), we found sodium bicarbonate most satisfactory. A stream of carbon dioxide passed through the system serves to agitate during exposure, to remove oxygen, and to maintain a constant pH.

From "aging" tests at room temperature it appeared that the rate of change (coalescence of particles, growth by recrystallization, etc.) was very slow even over 60 hours. Sols of the same age appeared very reproducible; they were used usually at 30 minutes. The specific surface could be controlled by observing the amount of the basic dye (IVb) required for saturation. On adding slowly a solution of this dye, at saturation all the sol is coagulated, and a solution free from color is obtained. It was found that 18 mg of dye were adsorbed per 1 gram of silver bromide. By comparison with the amount adsorbed to grains

[6] F. Weigert and F. Lühr, Z. wiss. Phot. **27**, 312 (1930).

* Using red or infra-red radiation, to which the silver halide is transparent.

† $[Ag]_a = kD$ (silver bromide sol)
$[Ag]_b = kD+\Delta$ (silver bromide emulsion)
The photometric constant k is the same; the intercept in case (b) represents density due to pre-exposure silver and silver sulfide nuclei.

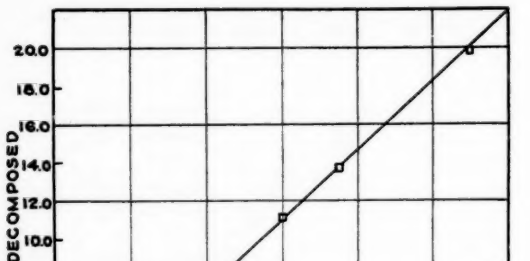

FIG. 1. Decomposition of dye on AgBr hydrosol by exposure to light. Erythrosine pH = 7.6, Temp. = 26°C. ⊙ = lamp 61.5 cm from reaction vessel; △ = lamp 30 cm from reaction vessel; ⊡ = lamp 15 cm from reaction vessel.

of an emulsion of known surface[1] and noting that this amount was 1/15 of that taken up by the sol particles, the average diameter of these was estimated as 0.18μ which agrees reasonably with the data of Bokinik and Iljina. There were very few microscopically resolved particles, i.e., above 0.25μ. With excess silver ions the sol was only stable at quite low pH values; with excess bromide ions at pH values of 6 and upward it was very stable.

PHOTODECOMPOSITION OF ADSORBED ERYTHROSINE

A silver bromide sol as described, containing 3.76 g silver bromide was sensitized with 25 mg of erythrosine and was exposed to light in a parallel-faced glass cell of about 2000 cc capacity, height 20 cm, width 13 cm and depth 9 cm. This was enclosed in an air thermostat at 25°C, and illuminated through an aperture of 10×10 cm. The light source was an H3 mercury arc* operating at 100 atmospheres pressure for maximum intensity. This gives an Hg line spectrum, superimposed on a continuous background spectrum. The line at 546 mμ is quite intense, though somewhat pressure broadened. To isolate this the diaphragm was covered by a No. 77 Eastman filter plus one sheet of No. 15 filter. These filters cut rather sharply at 500 mμ, but some radiation absorbed by plain silver bromide passes, since a small amount of silver was formed when an undyed sol was exposed to the filtered radiation. The energy incident was determined with a (calibrated*) photronic cell. With the filters, the incident energy entering the cell, over 100 cm^2, was found to be $1.33 \mp 0.16 \times 10^{17}$ quanta per second. This would be mostly at 546 mμ, although, as has been stated, there is some extraneous radiation.

The sol was stirred mechanically, with thorough agitation, so that all particles on an average were brought to the front of the cell, where the illumination is highest, over a quite short cycle. To follow the effect of light on the dye, samples were removed from time to time, the silver halide dissolved in thiosulfate solution, the dye extracted with butyl alcohol, and determined in the colorimeter or spectrophotometer.

Under these conditions, the dye is decolorized progressively with time of exposure as shown in Fig. 1. The curves show results obtained at three different distances of the lamp. (The source was far from being a point source, so that it would not give a $1/d^2$ intensity. On the other hand, the luminous area was not sufficiently comparable with that illuminated to give a $1/d$ intensity.)

On changing the concentration of dye, the proportional decomposition was much the same for 20 and 25 mg dye per liter, but fell off greatly—and indeed absolutely for 50 mg. It is probable that this was due to shielding action of unadsorbed dye, which is not decolorized. Dye adsorbed to barium sulfate was also not decolorized. Some measurements were made of the yield of silver produced; the results were rather erratic, but indicated 1 to 2 atoms of silver per dye molecule decolorized. This was not pursued further under these conditions.

Similar results were obtained with silver halide sensitized with basic dye, in that, qualitatively, the dye adsorbed to silver bromide, was bleached in light absorbed by the dye.

These results at first might seem to support a chemical theory of optical sensitizing according to which the dye on absorption of light reduces

* General Electric Company.

* Our thanks are due to Dr. J. H. Webb of these Laboratories.

the silver halide, but is itself decomposed. However, on exposing dyed silver bromide to blue-violet light, which was *not* absorbed by the dye, but by the silver bromide itself, the dye was equally decolorized, and silver produced. It then appeared probable that the dye was not directly decolorized by light, but in a purely secondary reaction, by the halogen liberated.

That this is the case seemed proved by carrying out the previously described experiment, but with a halogen acceptor present. With 0.1 g of acetone semi-carbazone per liter, exposure under similar conditions for 18 hours showed no decolorization of the dye, although a considerable amount of silver was produced. Other halogen acceptors were also effective, and in a number of later experiments *phenol* was used, since it does not react with iodine. Gelatin is also to a certain degree an effective halogen acceptor, so that conditions in the photographic film or plate resemble those now introduced.

Bokinik and Iljina[5] make no mention of a halogen acceptor, nor of decolorization of the dye. For these and other reasons it is not useful to compare our results with theirs.

The function of a halogen acceptor in protecting the dye was later found to be less simple than as first thought. On adding bromine slowly in dilute solution to a solution of dye and a halogen acceptor, it was observed that the dye was decolorized. If, as soon as this happened, no more bromine was added, the color returned, and the dye was recovered unchanged. A similar result was obtained by adding a solution of the brominated, decolorized dye to a halogen acceptor. Again the dye was regenerated. The brominated dye added to a silver sol was also regenerated, with production of silver halide.

The amplification and more detailed investigation of this phenomenon will be discussed elsewhere. But in regard to the mechanism of optical sensitizing, it is evident that important secondary reactions are:

i. Dye$+x$ Br (or Br_2)$\rightarrow$Dye $(Br_2)_x$
ii. Dye $(Br_2)_x+x$ Acc.$\rightarrow$Dye$+x$ (Acc. Br_2).*

Since the brominated dye is optically inactive, the photolytic activity of the dye molecule will be *partly conditioned* by the velocities of the reactions (i) and (ii), and by the temperature coefficients of these reactions.

* Or Acc. Br+HBr.

Photochemical Yield and Adsorption-Density

Varying amounts of erythrosine were incorporated in a gelatino-silver bromide emulsion containing 3.6 g/100 cc of silver bromide but no other sensitizing dye. After thorough agitation during time for adsorption to complete, 100 cc was removed and diluted to 1000 cc, and exposed in the apparatus already described. Twenty-five cubic centimeter samples were removed from time to time, and analyzed for reduced silver by the photometric method. The results are plotted as curve I in Fig. 2. Other 500-cc amounts of the same emulsion containing different amounts of erythrosine were coated on glass plates, dried and exposed to the light of the 546-mμ line of the mercury arc, the exposures being only sufficient to form a latent image. After development the characteristic curves were plotted and the speeds determined as $10/i$ values, where i is the inertia. The values are plotted for comparison on the same graph as the photolytic yields, in curve II, Fig. 2.

It will be noticed that the curves are very similar in shape, and that the maximum of the photographic sensitivity occurs at nearly the same value of added erythrosine as that of the photochemical yield. The amount of dye added to unit volume of emulsion is not a completely significant value; it is rather the amount of dye

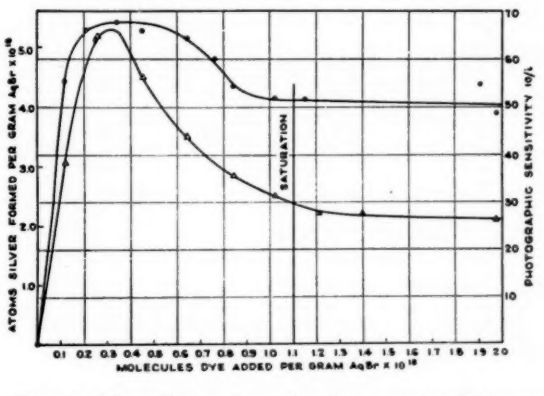
ATOMS SILVER FORMED PER GRAM AgBr x 10^18
PHOTOGRAPHIC SENSITIVITY 10/i
SATURATION
MOLECULES DYE ADDED PER GRAM AgBr x 10^18

Fig. 2. The effects of erythrosine on photolytic and photographic sensitivity. ○ = photolytic sensitivity; Δ = photographic sensitivity.

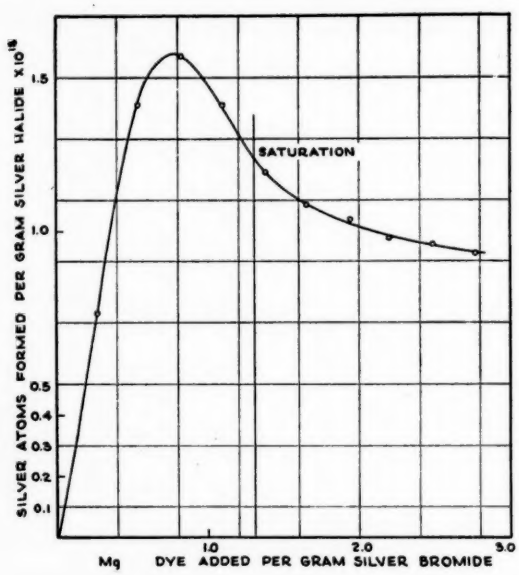

FIG. 3. Photolytic Yield with dye IVb. Temp. 25°C; pH = 6.8.

adsorbed which is the true independent variable. We have not succeeded so far in getting very satisfactory values for the adsorption of erythrosine to sol particles of silver bromide, because of the difficulty of separating the intramicellar liquid from the colloid.* However, with the emulsion in question, the dyed silver halide particles could be separated centrifugally, and the adsorption measured, as described previously. The *saturation* reached in these experiments may not represent maximum possible coverage, because the pAg of the emulsion was about 8, i.e., there was some excess bromide ion. Adsorption of *acid* dyes increases, to a limit, with increasing silver ion, i.e., decreasing pAg. The data on photochemical yield and photographic sensitivity when plotted against adsorption, show that both the photolytic yield and the sensitivity reach a maximum at about only 20 percent of saturation, and this may not represent full coverage. We have found that a similar advance to a maximum before adsorption saturation is obtained with basic dyes, though in the examples studied the maximum was only reached for a considerably larger fraction of the surface saturation, of the order of 60 percent (cf. Fig. 3).

* Experiments with ultra-filtration are in progress.

THE QUANTUM EQUIVALENT

The quantum equivalent is the number of atoms of silver produced per quantum of light absorbed by the adsorbed dye. The investigations of Eggert and Noddack,[7] of Kieser,[8] and of Meidinger[9] have shown rather conclusively that for blue-violet light* absorbed by silver bromide itself, initially one silver atom is produced per quantum absorbed. There are no measurements recorded which would enable this value to be calculated for optically sensitized silver halide. The experiments of Lescynski[4] and of Tollert[10] only refer to quanta incident, not to quanta absorbed. To estimate values of the absorption in these cases is very difficult, because there was an unknown excess of unadsorbed dye.

Since with the basic cyanine dyes so far studied the adsorption is irreversible and complete below the primary saturation level[1] it is a simplification to use these.† The following investigation was carried out with dye IVb and a silver bromide emulsion in gelatin, termed No. 1008 for record. This combination shows two sensitizing bands, one with a maximum at 540 mμ, and the other at 590 mμ. The experiments at 590 mμ are described since they were more complete.

The cell used was circular in section, having an internal thickness of 4.76 mm between front and

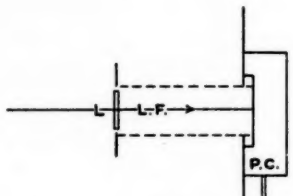

FIG. 4. Schematic diagram of cells in position during exposure. *L.* Light source; *L. F.* light flux; *P. C.* photronic cell or (alternative) photochemical cell.

back parallel glass plates, and an internal diameter of 76.2 mm. It was mounted just outside the lamphouse of an H3 mercury lamp. Between

[7] J. Eggert and W. Noddack, Zeits. f. Physik **31**, 922 (1925).
[8] H. Kieser, Zeits. f. wiss. Phot. **26**, 275 (1929).
[9] W. Meidinger, Physik. Zeits. **38**, 564 (1937).
* And near ultraviolet.
[10] H. Tollert, Zeits. f. physik. Chemie **140A**, 355 (1929).
† This statement must not be regarded as extended to all cyanine dyes.

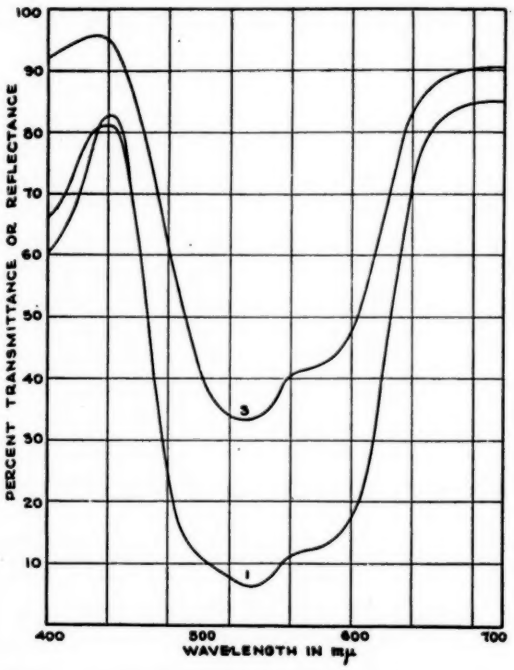

FIG. 5. Comparison photometric (curves) of dyed to undyed emulsion. 1. relative transmission. 3. relative reflection.

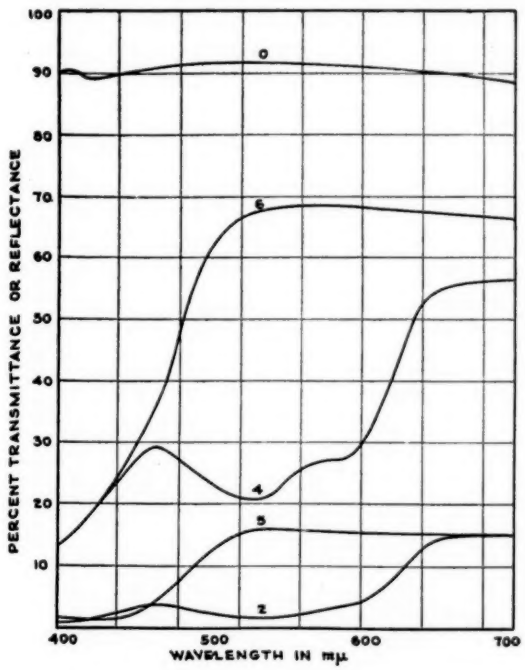

FIG. 6. Direct photometric measurements for absorption. 0, transmission, cell with water. 2, transmission, cell and dyed emulsion. 4, reflection, cell and dyed emulsion. 5, transmission, cell and undyed emulsion. 6, reflection, cell and undyed emulsion.

the cell and the light source was a combination of Eastman No. 22 filter, and one of copper acetate in gelatin on glass. This combination transmits a fairly narrow band of average wave-length 590 mμ; it is sharply cut at 554 mμ to prevent any light at 546 mμ from passing. Entrance and exit ports allowed the emulsion, diluted 1 : 10 with water, to be circulated continuously through the cell during exposure.

In Fig. 4 is shown schematically the set-up of the exposure-cell, *C*, and a photronic cell *P. C.* as used to measure the incident light-flux. *L* is the H3 high pressure mercury capillary lamp. The light source is a column 19 mm long and about 2 mm wide; it was placed 15 cm from the aperture. This was 19 mm in diameter. The sensitive face of the photronic cell was 38 mm in diameter, and the light-flux, *L. F.* thus covered somewhat more than 25 percent of its total sensitive area. Since the light-sensitive face of the photronic cell is set back somewhat from the aperture (about 3 mm) it is not at the position of the surface of the emulsion, which may cause a small error.

The photronic cell was calibrated against a thermopile, with a monochromator as illuminator. The cell has fairly uniform sensitivity over the range 500 mμ to 600 mμ. The radiation equivalent of the thermopile in ergs was known, and it was found that 2.74×10^{-8} ampere at the photronic cell was equivalent to 16.2 ergs per second of radiation at 546 mμ. Hence, if A = amperes from the photronic cell, and t = time in seconds, the incident light-flux

$$I_0=\frac{A\times16.2\times t}{2.74\times10^{-8}}\text{ ergs.}$$

MEASUREMENT OF ABSORBED ENERGY

The determination of the light absorbed in the suspension of silver halide particles is complicated by the scattering between phases of different refractive index. The measurements were made with a Hardy color analyzer which is a photoelectric recording spectrophotometer, employing an integrating head; percentage reflection and transmission values, relative to incident light may be measured by comparison with a reflectance standard. In Fig. 5 are given the graphs for the

reflection and transmission of the dye sensitized (liquid) emulsion in the cell in comparison with undyed emulsion.

In Fig. 6 are shown data on the actual percentages of light reflected and transmitted for the cell filled (a) with water, (b) with undyed emulsion, (c) with dyed emulsion.

Measurements were made of a strip of motion picture positive film in position. This was quite thin. It was then rephotometered between glass plates of the same thickness as those of the cell. Similar measurements were made with the cell content of undyed emulsion dried down on a glass plate and faced by another glass plate.

The sum of directly reflected and transmitted light subtracted from the incident light gives the light absorbed and scattered. It was found that for the thin film, with no glass, the absorption is practically nil at wave-lengths longer than the absorption limit for the silver halide, whereas with the cell in position an apparent absorption of 17.5 percent was observed at the same wave-lengths. This loss is scattered and deviated light escaping the sphere. As stated, the quantities involved may be written

$$I_0 = I_T + I_R + I_S + I_A,$$

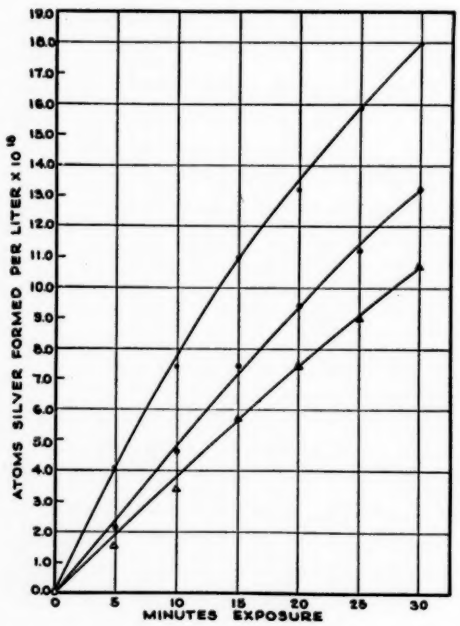

FIG. 7. Growth of silver formed with exposure. ●=5.0 mg erythrosine/L; ○=10.0 mg erythrosine/L; Δ=12.5 mg erythrosine/L.

where T refers to transmission as measured, R refers to reflectance as measured, S refers to scatter loss, A refers to absorption. From curves 4 and 2 of Fig. 6 the reflected and transmitted lights for dyed emulsion are 27.5 percent and 3.0 percent, respectively. At 700 mμ there is no absorption, $I_A=0$, while $I_T=15$ percent, $I_R=55$ percent. Hence, at 700 mμ $I_S=29.0$.

Assuming that all light not directly transmitted or reflected at 700 mμ is scatter loss, and that the

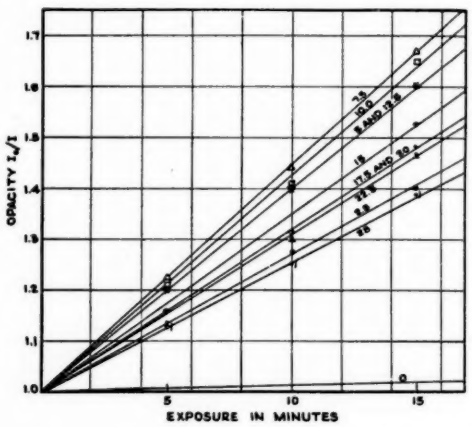

FIG. 8. The opacity of silver produced as a function of exposure. Numbers denote mg of dye IVb per 200 cc emulsion (9 grams silver halide).

scatter loss is the same at 590 mμ, on substituting in the equation we have

$$I_0 = 27.5 + 3.0 + 29.6 + I_A = 100.$$

Whence $I_A=40.5$ percent. This may be checked independently by the data of curves of Fig. 5—giving reflections and transmissions of dyed emulsion relative to undyed—and using *5* and *6* of Fig. 6. At 590 mμ there is 13.5 percent incident light transmitted referred to undyed emulsion, and 43.5 percent *relatively* reflected. Now undyed silver halide (in the cell) reflected 67 percent light incident, and transmitted 15.5 percent. Hence,

$$I_R \text{ (dyed)} = 0.67 \times 43.5 = 29.1$$
$$I_T \text{ (dyed)} = 0.135 \times 15.5 = 2.1.$$

At 700 mμ by a similar calculation, I_S is found to be 27 percent. Assuming this for 590 mμ we have

$$100 = 29.1 + 2.1 + 27 + I_A,$$

whence $I_A=41.8$ percent, which checks the value

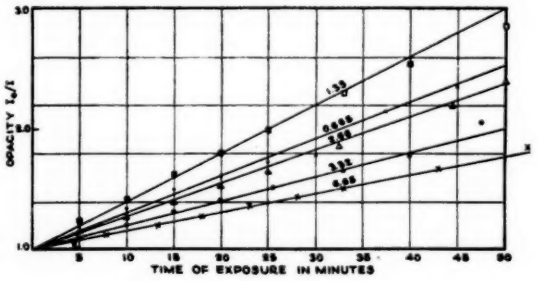

FIG. 9. The opacity of silver produced as a function of exposure. Numbers denote mg erythrosine per gram silver bromide.

40.5 percent reasonably well. It may be noted that the light loss by reflection and scattering with the cell and water automatically cancels out. It is now considered that with some alteration of the position of the cell more reliable values—and less loss from scatter—can be obtained, but pending these new experiments we shall take 41 percent as the absorption at 590 mμ by the dye used in the experiments here described.

THE QUANTUM YIELD

The incident light flux, by the energy measurements given

$$=\frac{A\times 16.2\times t}{2.74\times 10^{-8}}\text{ ergs},$$

where A = amperes on the photronic cell, t = time in seconds; multiplying by the fraction 0.41 gives the absorbed energy in ergs. From the equation $\epsilon=h\nu=hc/\lambda$ ergs per quantum

where $h=6.547\times10^{-27}$ (Planck's constant)
$c=3\times10^{10}$ cm/sec. (velocity of light)
$\lambda=5.9\times10^{-5}$ cm (wave-length),

the absorbed light in quanta is

$$I_a=\frac{A\times 16.2\times 60\times 0.41}{2.74\times10^{-8}\times 3.33\times10^{-12}}=\frac{\Delta Q}{\Delta t}$$

quanta absorbed per minute.

THE PHOTOLYTIC SILVER YIELD

When the silver formed is plotted as a function of time of exposure, i.e., as function of quanta incident, convertible to quanta absorbed by the foregoing expression, curves are obtained as shown in Fig. 7. The values of the quantum equivalent decrease steadily with the exposure, as would be expected from the shielding effect of the silver produced, and, as will be shown in a later publication, from the insufficiency of the halogen-accepting capacity of the gelatin after a small amount of photolysis has taken place. Hence, the values do not correspond to the primary or elemental process.

It might be supposed, as a first approximation, that the rate of silver formation could be represented by an equation of the form

$$\frac{d[\text{Ag}]}{dt}=kIa\,f(\text{dye})\,[\text{Ag}_{\text{lim}}-\text{Ag}]$$

where, I = intensity of light,
a = area of silver halide adsorbing dye molecules,
f(dye) = function of adsorption-density,

and $[\text{Ag}]_{\text{lim}}$ is the limiting amount of silver or silver halide, [Ag] the amount of silver formed up to the time t. A principal difficulty is the estimation of $[\text{Ag}]_{\text{lim}}$. Taking total silver bromide in the suspension gives values which are apparently far too high. On the other hand, the surface atom layer, calculated from the specific surface, gives quantities considerably lower than that actually obtained on prolonged exposures. There is also evidence from Lescynski's work that considerable silver is formed in the interior of the grains. (We have confirmed this in one experiment, but plan further work on this distribution factor.) Attempts to evaluate $[\text{Ag}]_{\text{lim}}$ empirically by an integrated form such as

$$K=1/t\log\frac{[\text{Ag}]_1}{[\text{Ag}]_2-[\text{Ag}]_1}\quad\text{for}\quad t_2=2t_1$$

gave values too variable to be acceptable. It was

TABLE I.

EXPERIMENT	k	A	$\Delta Q/\Delta t$	$\Phi=\frac{k}{\Delta Q/\Delta t}$
1	2.25×10^{16}	5.2×10^{-6}	2.27×10^{16}	0.992
2	2.25×10^{16}	6.6×10^{-6}	2.88×10^{16}	0.782
3	2.9×10^{16}	5.2×10^{-6}	2.27×10^{16}	1.280
4	1.82×10^{16}	5.2×10^{-6}	2.27×10^{16}	0.801
5	2.9×10^{16}	5.5×10^{-6}	2.4×10^{16}	1.21
6	2.47×10^{16}	4.5×10^{-6}	1.97×10^{16}	1.25
7	1.04×10^{16}	2.5×10^{-6}	1.092×10^{16}	0.952

then found that the reaction curves could be represented with considerable accuracy by the equation

$$10^D = kt+1,$$

where, D is the photometric density of the silver formed, and which, as shown previously, is related to [Ag], the silver by simple proportionality, [Ag]=constant$\times D$, k is a constant, and t is the time of exposure. This expression is also readily handled in the form

$$D=\log\,(kt+1).$$

In Fig. 8 are shown the results of experiments with the silver bromide emulsion No. 1008 for various amounts of dye IVb adsorbed to the grains. We have plotted here $I_0/I=10^D$ as a function of $kt+1$, which is linear over the range studied. We obtained confirmatory results (cf. Fig. 9) for exposure of a pure silver bromide sol sensitized with erythrosine, and having only a small amount of auxiliary halogen acceptor present (phenol). This function seems to represent the course of the reaction quite well when the amount of halogen acceptor present is just sufficient to preserve the dye for about 1 percent decomposition. From this we can obtain the initial rate. Since

$$\frac{d[\mathrm{Ag}]}{dt}=\frac{d\,\log\,(kt+1)}{dt}=\frac{k}{kt+1},$$

then

$$\left(\frac{d[\mathrm{Ag}]}{dt}\right)_{t=0}=k,$$

i.e., k is the initial rate of formation of silver. The initial quantum equivalent Φ is then obtained as $\Phi=k/\Delta Q/\Delta t$, the values of k and $\Delta Q/\Delta t$ referring to the same time unit. In Table I are given the results for duplicate runs on a dilute emulsion containing 4.52 g AgBr per liter and 2.5 mg of dye IVb. The dye was insufficient to cover the grains, the coverage, in fact, being of the order of 25 percent of saturation.

The average value for the initial *quantum equivalent* is 1.04 ∓ 0.18. This deviation is the average and may seem large, but the uncertainty of the absorption measurements is estimated at 10 percent, and the constancy of the light intensity was not much better. The results,

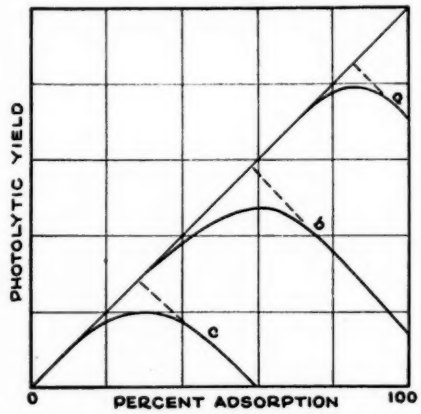

FIG. 10. Schematic comparison of sensitizers.

however, indicate a very strong probability that the initial quantum equivalent, corresponding to the elemental reaction

$$D_{\mathrm{Br}^-}^{\mathrm{Ag}^+}+h\nu=D+\mathrm{Ag}+\mathrm{Br}$$

is unity, i.e., for the reaction uncomplicated by shielding, recombination, etc. Inasmuch as the investigation was made for an absorption, i.e., sensitizing, band corresponding to what is believed to be an aggregated, or according to Scheibe[11] a polymerized form of the dye, the result argues against Scheibe's suggestion that in such aggregated forms two or more quanta of lower magnitude, e.g., at 590 mμ, might be compounded to produce a quantum of higher magnitude, sufficient normally to decompose silver bromide.

The progressive fall of the quantum yield, i.e., the efficiency, with time of exposure, is caused both by shielding (absorption of effective light by the silver produced) as well as by recombination due to deficiency of halogen acceptance. In later experiments these have been largely corrected, and the progressive photolysis in the optically (dye) sensitized region brought more in line with that observed for silver bromide alone in blue-violet light in the presence of adequate halogen acceptors.[9]

On the other hand, the fall in efficiency—beyond a maximum—with increased adsorption density of dye, together with the existence of an optimum before saturation is reached, remains to

[11] G. Scheibe, Zeits. f. angew. Chemie **49**, 563 (1936).

be explained. Where, as frequently happens, two or more absorption and sensitizing bands are shown on silver halide, these begin to appear at low adsorption densities[1] and remain up to saturation, with displacement. Moreover, the aggregated or polymerized form of the dye does not appear in aqueous solution, but only by way of adsorption to the halide. The existence of an optimum was formerly attributed[3] to shielding action of unadsorbed dye once saturation was reached. However, in our experiments both with an acid dye, erythrosine and with basic dyes, the evidence was very definite that optimum sensitizing was reached well *before* saturation. Experiments of Leermakers, Carroll and Staud[12] indicated that with three cyanine dyes the optimum sensitizing concentration, on change of specific surface, was proportional to the specific surface (over a range of 1 to 3). Hence, if optimum sensitizing does not occur at saturation, it appears for the same dye to occur for a constant fraction of saturation. Now the "desensitizing effect" of dye beyond the optimum is much more abrupt and considerable than would be expected from shielding by unadsorbed dye. Moreover, it frequently occurs at still lower concentrations in respect of the "blue" sensitivity, though sometimes at the same value as for the optical sensitivity. All in all, it appears that we must admit a true "desensitizing," only brought about by the adsorbed dye. This agrees with our observation that optimum photochemical yield, and optimum photographic sensitizing occur considerably before saturation and at about the same point.

There is considerable evidence that optically sensitizing dyes vary both in their sensitizing efficiency and in their desensitizing ability.[13] There is also evidence that certain pronounced desensitizing dyes can act to some extent, and under certain conditions—notably with silver iodide—as optical sensitizers. In terms of the density of adsorption (percentage saturation) we might express the facts diagrammatically by Fig. 10.* Here (a) is a powerful (optical) sensitizer, showing very slight desensitizing, (b) is a fair sensitizer, showing considerable desensitizing at higher concentrations, (c) is a very weak sensitizer, soon showing desensitizing properties.

The question arises, to what can we assign this ambiguity of function? It seems to us very probable that it is determined by the *halogen accepting and donating property of these dyes.* We have mentioned already that these dyes are both very active halogen acceptors and halogen donors. Brominated dyes rapidly brominate colloidal silver. If we consider part of the surface of a silver halide grain covered with adsorbed dye —probably in patches—the remainder covered with an adsorbed halogen acceptor, such as gelatin, which can take up halogen more slowly but more permanently than the dye, it appears feasible that up to a certain partition of the surface, the dye, halogenized through its photolytic effect on the silver halide, can transfer its halogen to the accessory acceptor, thus becoming regenerated optically, while recombination is prevented. As the surface approaches saturation, this transfer becomes increasingly difficult, and recombination is facilitated. This explanation is made more plausible by the relatively large amounts of bromine which can be reversibly combined with a dye molecule. More extended data will be given elsewhere, but as an example it is found that *pinacyanol* can take up six atoms, or three molecules, of bromine. This explanation, while plausible for the "sensitizing optimum," does not in itself explain the weaker or deficient optical sensitizing effect of the better "desensitizers." For this, further study is necessary of both the halogen transfer function, and of the inner mechanism of optical sensitizing.

The Inner Mechanism of Sensitizing

The evidence for a primary quantum equivalent of unity does not itself indicate what the mechanism of sensitizing may be. We have shown that decolorization and chemical change of the dye are only indirect and transient consequences of the photolysis. A further fact of importance is that we have recently obtained in this laboratory very definite evidence for release of electrons from dye sensitized silver halide which produce pronounced inertialess photo-

[12] J. Leermakers, B. H. Carroll and C. J. Staud, J. Chem. Phys. **5**, 893 (1937).
[13] Lüppo-Cramer, Zeits. f. wiss. Phot. **30**, 1 (1931).
* This is certainly an excessive simplification, and other representations are possible.

voltaic effects[14] on illumination by the light absorbed by the dye. But while the evidence is definite for the production of internal conducting photoelectrons, this does not specify their origin. As to this there appear at present two types of mechanism conceivable:

a. The adsorbed dye-molecule, or—in the case of an aggregated form—the dye complex emits at the crystal interface one electron on absorption of one quantum. This electron is accepted somewhere in or on the silver halide crystal by a silver ion. (From latent image studies the mechanism of concentration, whatever this may be, appears to be the same for normal and optically sensitized latent image formation.) Furthermore, by some means not clear, the dye, having lost an electron from its resonance chain, is able to regain one from a bromide ion of the lattice. This is the type of mechanism supported by Gurney and Mott[15] but it begs the question as to the regain of the electron.

b. The light excited dye-molecule, or complex, transmits sufficient energy to a bromide ion of the silver halide to displace an electron into the conductance level of the crystal. The mechanism of such energy transfers in crystals has been discussed recently by Franck and Teller.[16] But whatever the mechanics of the migration of the energy, the problem now remains as to the restoration of the dye molecule (or complex) to its original level from that to which it would have fallen by the transaction. Possibly this may be partly restored by thermal activation; or again in part on transferring halogen to a more retentive acceptor.

Of the two conceptions, the energy transfer seems at present preferable to the direct emission of photoelectrons. Possibly the difference between the two concepts is not significant. But, in any case, we wish to stress the importance of the bromide ion partner in the transaction, as exemplified in the case of erythrosine. We have observed that the spectral absorption of silver bromide dyed with erythrosine is identical with that of solid silver erythrosinate, which differs considerably from that of erythrosine (acid) or of the sodium compound, the maximum being displaced toward the red about 40 mμ. This indicates a rather close bonding of the silver ion with the dye anion. It is probable then that the absorber, and the absorption act, are the same for (solid) silver erythrosinate and for the dye adsorbed to silver bromide. Yet on exposure of pure silver erythrosinate to light (in its own absorption band) no photolysis could be detected up to exposures which with the dyed silver bromide produced considerable metallic silver, and freed equivalent bromine.* Apparently, therefore, combination in a crystal lattice with silver bromide enables the quantum of energy absorbed by a monolayer of silver erythrosinate to decompose silver bromide, with freeing of electrons, although the same quantum of energy absorbed by solid silver erythrosinate alone remains short-circuited, without photochemical effect. This rather suggests—but does not necessitate—that the energy absorbed by the dye is transferred integrally to a bromide ion, and that this is the source of the free electron observed in the photovoltaic effect.

It is believed that studies of the temperature coefficients of the photolysis now in progress, and of such of its partial or secondary components as can be isolated, will help to throw further light on the nature of the mechanism. This is being supplemented by investigation of the partition of the photolytic silver between the interior and the exterior of the grains.

[14] S. E. Sheppard and W. Vanselow, J. Phys. Chem. **33**, 331 and 1403 (1929).
[15] R. W. Gurney and N. F. Mott., Proc. Roy. Soc. **164A**, 151 (1938).
[16] J. Franck and E. Teller, J. Chem. Phys. **6**, 861 (1938).

* Some darkening occurs on very intense illumination but this is probably due to decomposition by heat.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Internal Rotation in Dimethyl Acetylene

A preliminary comparison of calculated and observed heat capacities for gaseous dimethyl acetylene indicates that the internal rotation of the methyl groups against one another is essentially free, the restricting potential barrier being less than 500 cal./mole. This result agrees with that expected from the large distance between methyl groups.[1]

A study of the infra-red and Raman spectra of this molecule, to be published soon by one of us, gives a basis for the calculation of the heat capacity for the ideal gas, C_p^0, exclusive of the contribution from the internal rotation, C_r. This quantity $(C_p^0 - C_r)$ is compared with the other data in Table I.

Measurements on the heat capacity of the gas have been made by the adiabatic expansion method recently described.[2] The values of C_p' obtained are given in Table I. In order to correct C_p' to C_p or to C_p^0, it is necessary to use equation-of-state data. Since these are not available for dimethyl acetylene, the following procedure was used to obtain an estimate of the correction. A plot of critical pressure *vs.* critical temperature was made for a number of hydrocarbons; the plot showed satisfactory regularity, and was used to obtain the critical pressure of dimethyl acetylene from the known critical temperature.[3] These critical data were then used in the Keyes equation[4] to evaluate the correction $(C_p^0 - C_p')$. As a check on the reliability of the results, the same method was used for a number of hydrocarbons for which equation-of-state data are available; the comparisons with the known values indicate that the corrections $(C_p^0 - C_p')$ for dimethyl acetylene are probably good to 0.10 cal./mole degree.

The resulting values for C_r, the contribution from the internal rotation, are consistent with the value 0.99 cal./mole degree expected for a completely free motion; i.e., a restricting potential of 0. Using the data at 369°, with the limit of error of 0.12 cal./mole degree indicated, a maximum value of 500 cal./mole is found for the restricting potential. (Values from Pitzer's tables[5] were used.)

The validity of this result depends on the correctness of the vibrational assignment used in calculating $(C_p^0 - C_r)$ as well as on the accuracy of the correction for gas imperfection. A study of the heat capacity of the gas over a wider temperature range, using the hot-wire method,[6] is now in progress; it is hoped that this work will serve to check the vibrational analyses and the correction used here, and to determine the restricting potential more accurately.

TABLE I. *Heat capacity data for gaseous dimethyl acetylene, in cal./mole degree.*

T, °K	$(C_p^0 - C_r)$	C_p'	$(C_p^0 - C_p')$	C_p^0	C_r
336	19.14	19.41±0.03	0.80±0.10	20.21±0.11	1.07±0.12
369	20.47	20.76±0.04	0.67±0.10	21.43±0.11	0.96±0.12

In concluding, we wish to thank Professors G. B. Kistiakowsky and E. B. Wilson, Jr. for their continued interest in this work and for many helpful contributions thereto.

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May 12, 1939.

[1] See, for example, G. B. Kistiakowsky, J. R. Lacher, and W. W. Ransom, J. Chem. Phys. **6**, 900 (1938).
[2] G. B. Kistiakowsky and W. W. Rice, J. Chem. Phys. **7**, 281 (1939).
[3] F. R. Morehouse and O. Maass, Can. J. Research **11**, 640 (1934).
[4] F. G. Keyes, J. Am. Chem. Soc. **60**, 1761 (1938).
[5] K. S. Pitzer, J. Chem. Phys. **5**, 471 (1937).
[6] G. B. Kistiakowsky, J. R. Lacher, and F. Stitt, J. Chem. Phys. **7**, 289 (1939); and references therein.
* National Research Fellow in Chemistry.

Errata: The Electrostatic Influence of Substituents on the Dissociation Constants of Organic Acids. I and II

(J. Chem. Phys. **6**, 506, 513 (1938))

The title of Table II, p. 511 should read "Values of $\sqrt{x}D_E(x)$." Eq. (2), p. 514, should contain the factors $[1-(D_i/D)C_n]^{-1}$ rather than $[1+(D_i/D)C_n]^{-1}$. Similarly, the negative sign is proper in the corresponding term of Eqs. (3), (14), (17) and (18), pp. 514, 516 and 517. Further, Eq. (2) should read

$$U_n = 2(2n+1)\frac{Q_n(\lambda_0)}{P_n(\lambda_0)}(-1)^n$$

and Eq. (3)

$$Y_n = -2n(n+1)(2n+1)\frac{Q_n(\lambda_0)}{P_n(\lambda_0)}(-1)^n.$$

In Eq. (19), $(-1)^n$ rather than $(-1)_n$ should appear. The correct equations were employed for the numerical calculations.

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May 2, 1939.

The Vapor Pressures of *o*- and *p*-H_2 and D_2*

In a recent article on the vapor pressures of *o*- and *p*-hydrogen and *o*- and *p*-deuterium,[1] the derivation of the differences in sublimation-heats[2] (ΔE) was stopped at the differences in attractive potentials (ΔE_A). It was remarked that the step from ΔE_A to ΔE could not be made without a knowledge of the relation between E, E_0 (the zero-point energy), r, E_A and E_R (the repulsive energy). The timely publication of such a relationship by Hobbs[3] enables us to complete our argument. We have

$$E=-E_A+E_R+E_0, \tag{1}$$

where E_0 is given by[3]

$$E_0=\frac{Cd}{(r-d)^2(r+0.800d)} \tag{2}$$

with r the intermolecular distance; d, a molecular radius determined from the repulsive forces (=2.70A); C, a constant. The equilibrium condition is

$$E'(r)=0. \tag{3}$$

From (1) and (3) we find

$$\Delta E=-\Delta E_A(r)+\Delta E_0(r), \tag{4}$$

$$\Delta E\equiv E_{o\text{-}H_2}-E_{p\text{-}H_2} \tag{4a}$$

or

$$\Delta E\equiv E_{p\text{-}D_2}-E_{o\text{-}D_2}, \tag{4b}$$

the value of r in (4) being determined by (3). In calculating the terms on the right-hand side of (4) it is understood that r is held constant.[4] E_0 depends only on the volume and the repulsive forces (through d). Since we are considering the repulsive forces to be held constant, $\Delta E_0(r)=0$ and $\Delta E=-\Delta E_A(r)$.

Taking $r=3.752$ and 3.573 (corresponding to $V=22.65$ cc and 19.56 cc of cubic close-packing) for H_2 and D_2, respectively, and recalculating from Eqs. (14) and (15) of our paper,[1] we find

$$\begin{aligned}&\text{for } H_2\text{: } \Delta E=-\Delta E_A(r)=-1.68 \text{ cal./mole}\\ &\text{for } D_2\text{: } \Delta E=-\Delta E_A(r)=-1.16 \text{ cal./mole.}\end{aligned} \tag{5}$$

We find experimentally that $\Delta E=-1.78$ cal./mole for both hydrogen and deuterium.

The volume change in passing from $o-H_2$ to $p-H_2$ can be shown to be

$$\frac{V_o-V_p}{V}=-\frac{18}{r^2}\Delta E_A(r)\frac{1}{E''(r)}$$

with r, as before, the root of $E'(r)=0$.

The volume change of the motionless solid ($E_0=0$) is likewise

$$\frac{V_o^0-V_p^0}{V^0}=-\frac{18}{R^2}\Delta E_A(R)\frac{1}{\phi''(R)},$$

where

$$\phi'(R)=-E_A'(R)+E_R'(R)=0.$$

It is evident that the much smaller value of $E''(r)$, compared to $\phi''(R)$, will give V_o-V_p a much greater value than $V_o^0-V_p^0$. This accounts for the difference between ΔV (observed) and ΔV^0 (calculated).[5]

Finally, we should like to take this occasion to correct two trivial errors in our paper.[1] On page 157, the upper limit of the last integral in Eq. (2) should be "∞" and not "T;" and in the last line of the same page, read "0.2 percent" instead of "0.1 percent."

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May 10, 1939.

* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.

[1] K. Cohen and H. C. Urey, J. Chem. Phys. **7**, 157 (1939).
[2] $-\Delta x$ in our previous notation.
[3] M. E. Hobbs, J. Chem. Phys. **7**, 318 (1939).
[4] Cf. K. Cohen and H. C. Urey, reference 1, p. 161.
[5] §§4 and 5, reference 1.

The Separation of Gases by Thermal Diffusion*

A simple approximate treatment of the case in which there are no complications due to convection will be presented later. It has the advantage that it can be easily worked out for mixtures containing any number of species. A result for the separation of two gases in the presence of others is as follows:

$$\frac{d\ln(x_1/x_2)}{d\ln T}=\frac{m_2-m_1}{2\Sigma m_i x_i}.$$

Here T denotes absolute temperature, x mole fraction, i any gaseous species (the summation is over all species), and m denotes the *square root* of the molecular weight.

The only data published are for binary mixtures. Comparison shows that the calculated separations agree well with the experimental in a few cases, fairly well in others (the calculated being higher) and are about double the experimental in the worst cases. The cases in which the lower temperature is extremely low are among the worst.

Interpretation of the equation suggests practical importance, since the separation of two heavier gases ought, according to it, to be improved by addition of a light gas such as hydrogen or helium. In the case of the separation of the isotopes 35 and 37 of chlorine by diffusion of hydrogen chloride, the maximum effect, as measured by the left-hand side of the equation, would correspond to a multiplication by four in the case of added hydrogen, three in the case of helium. The addition of helium might however be the more advantageous, since the agreement of the equation with data is poorest on the average for binary mixtures containing hydrogen and nearly the best for those containing helium.

The devices of Clusius and Dickel[1] and Brewer and Bramley[2] seem to act as ensembles of units in cascade, in which units ordinary thermal diffusion is taking place, and we may perhaps expect their operation to be susceptible of improvement by addition of light gas.

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May 8, 1939.

* Contribution No. 423 from the Research Laboratory of Physical Chemistry.

[1] Clusius and Dickel, Naturwiss. **26**, 546 (1938); **27**, 148 (1939).
[2] A. K. Brewer and A. Bramley, Phys. Rev. [2] **55**, 590(A) (1939).